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

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The parent tris(pyrazolyl)phosphine and its 3,5-Me2, 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 $^{1}J_{P,Se}$ 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-di-methylpyrazolyl)-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 Trofimenko1 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 chiral versions of OC ligands for asymmetric catalysis,11–14 while Weigand’s group applied tris(3,5-dimethylpyrazolyl)-phosphine (CMe$_2$) 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 $\kappa^3$ 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-
combined soft and hard binding sites.\textsuperscript{38} Janus-type ligands can be viewed as a Janus scorpionate ligand because of the heteroscorpionates akin to coordination polymers result when Ir complexes react with complexes\textsuperscript{39,40} and coordination polymers\textsuperscript{41} with the Co properties to generate a one-dimensional coordination polymer.

Fig. 2 A bimetallic complex supported by ligand D.

![Diagram of a bimetallic complex supported by ligand D.](image1)

Herein we present the synthesis of tris(pyrazolyl)phosphines \( \text{Se}^{\text{Bu}} \) to form the bimetallic complex (OC)\textsubscript{3} WDMo(CO)\textsubscript{3} (Fig. 2).\textsuperscript{22} We also showed that the two oxidized ligands OC and OD influence the coordinated metal similarly,\textsuperscript{21} 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,\textsuperscript{24} who used tethered, multitopic tris(pyrazolyl)methane ligands (Fig. 3a) with silver(I) complexes to generate an abundance of well-identified supramolecular structures,\textsuperscript{25–29} including argentachains with \( \kappa^2-\kappa^1 \) coordination modes (Fig. 3b).\textsuperscript{26,28} One-dimensional coordination polymers are also accessible by the embedded use of the position of the carbon atoms in its heterocyclic rings.

![Diagram of a bimetallic complex supported by ligand D.](image2)

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 \( ^1 \text{H} \) and \( ^{13} \text{C} \) NMR spectra revealed simple signal patterns, reflecting the expected equivalence of the three pyrazolyl groups; the \( ^{13} \text{C}(^1 \text{H}) \) NMR spectra showed the characteristic doublets (\( J_{C,P} \sim 10 \text{ Hz} \)) for the \( C^3 \) and \( C^5 \) carbons.

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

![Diagram of tris(pyrazolyl)methane ligands and complexes.](image3)

Results and discussion

Ligand synthesis

The known tris(pyrazolyl)phosphine \( \text{C}^\text{H} \) and tris(dimethylpyrazolyl)phosphine \( \text{C}^\text{Me}_2 \),\textsuperscript{8,9} and the new, more congested tris(3-phenylpyrazolyl)phosphine \( \text{C}^\text{Ph} \) and tris(3-tert-butylpyrazolyl)phosphine \( \text{C}^\text{Bu} \) were synthesized in modest to excellent yields using our recently reported protocol (Scheme 1).\textsuperscript{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 \( 0 \text{ °C} \), followed by prolonged stirring, either at room temperature for \( \text{C}^\text{H} \) and \( \text{C}^\text{Me}_2 \) or under reflux for the bulkier \( \text{C}^\text{Ph} \) and \( \text{C}^\text{Bu} \). The reaction progress was monitored by \( ^{31} \text{P} \) NMR spectroscopy using the characteristic singlet for the phosphorus apex of the products (\( \delta 61.1 \) (\( \text{C}^\text{H} \)), 72.0 (\( \text{C}^\text{Me}_2 \)), 60.2 (\( \text{C}^\text{Ph} \)), and 58.2 (\( \text{C}^\text{Bu} \))). After filtering off by-products and removal of the volatiles, colorless to yellow solids were obtained for which additional purification was only needed for \( \text{C}^\text{H} \) (recrystallization) and \( \text{C}^\text{Ph} \) (washings), reducing their isolated yields significantly. The \( ^1 \text{H} \) and \( ^{13} \text{C} \) NMR spectra revealed simple signal patterns, reflecting the expected equivalence of the three pyrazolyl groups; the \( ^{13} \text{C}(^1 \text{H}) \) NMR spectra showed the characteristic doublets (\( J_{C,P} \sim 10 \text{ Hz} \)) for the \( C^3 \) and \( C^5 \) carbons.

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![Diagram of a bimetallic complex supported by ligand D.](image4)

Ligand synthesis

Scheme 1 Synthesis of tris(pyrazolyl)phosphines \( \text{C}^\text{H} \text{–} \text{C}^\text{Bu} \).

![Diagram of a bimetallic complex supported by ligand D.](image5)

Scheme 2 Synthesis of tris(pyrazolyl)phosphine selenides Se\textsuperscript{H} and Se\textsuperscript{Me}_2.

![Diagram of a bimetallic complex supported by ligand D.](image6)
for selenophosphoramides, indicating \( C^{Me2} \) to be a weaker donor than, e.g., \( P(NMe_2)_3 \), \( J_{p,se} = 784 \text{ Hz} \) for the corresponding selenide.\(^{45}\) Unsubstituted \( C^H \) turns out to be a still weaker donor that compares better with weakly donating phosphonates \( (cf., \ J_{p,se} = 1025 \text{ Hz} \) for Se(P(Ph))\(_3\)).\(^{46}\) The weak \( \sigma \) 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 with copper(ii)**

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(i). 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(i) with acetonitrile completing the coordination sphere.\(^{20,47}\) For \( OC^{Me2} \), it has been 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 \( (cf., \ J_{p,se} = 735 \text{ Hz} \) for Se(P(Ph))\(_3\)).\(^{48}\)

Ideally, a head-to-tail Cu(i)-complex with \( \Delta CH_3CN \) solvent; the solid material was poorly soluble in common NMR solvents. It is interesting to note that, while the \( 1^C \) 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 \( [C^{Me2}Cu(NCMe)]PF_6 \), \( \Delta/J_{C,P} = \approx 8.5, \Delta/J_{C,P} = 4.3, \text{ and } \Delta/J_{C,P} = 20.4 \text{ Hz} \). Similar changes are observed for all complexes reported here (see the Experimental section). The observed \( 31^P \) NMR chemi-

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**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 \( [\text{Å}] \) and angles \( [\text{o}] \) for \([C^{Me2}Cu(NCMe)]PF_6\): Cu1–N12 2.077(3), Cu1–N14 1.888(3), P1–N11 1.713(3), P1–C1 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(5). 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 CMe2 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 [CMe2Cu(NCMe)2][PF6] with Na[BArF4] in CH2Cl2 gave in 57% isolated yield colorless [CMe2Cu(NCMe)][BArF4] that readily dissolves in solvents less polar than acetonitrile.

Its 31P NMR chemical shift at 20.0 ppm (CDCl3) compares with the complex having PF6− as the counterion (23.3 ppm; CD3CN), while the 1H NMR chemical shift at 2.23 ppm confirms the presence of the acetonitrile ligand.

The loosely bound acetonitrile of [CMe2Cu(NCMe)][PF6] could be exchanged for PPh3 upon stirring an equimolar mixture in CH2Cl2 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 1H and 13C NMR spectra. The 31P NMR spectrum showed in addition to the resonance for the CMe2 apex at δ 21.4 ppm one at δ 6.5 ppm for the new PPh3 ligand. Crystals obtained from CH2Cl2/pentane were suitable for a crystal structure determination by X-ray diffraction. The asymmetric unit showed two independent complexes with two CH2Cl2 molecules. Fig. 4 (right) displays one [CMe2Cu(PPh3)][PF6] complex. Its molecular structure confirms CMe2 as a tridentate ligand with PPh3 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 [OCMe2Cu(PPh3)][PF6]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 [CMe2Cu(PPh3)][PF6] 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 sera 4° more acute P–N angles.

As for CMe2, treating the more congested ligands CPh and CΦ-Bu with [Cu(NCMe)3][PF6] in either a unir- or a bimolecular ratio gives only the acetonitrile adducts [CPh,Cu(NCMe)][PF6] and [CΦ-Bu,Cu(NCMe)][PF6] in 56 and 43% isolated yields, respectively. Their 1H and 13C NMR spectra confirmed a 1 : 1 ratio of acetonitrile and the scorpion ligand. For both complexes the 31P NMR resonance of the P-apex is shielded by about 15 ppm compared to the free ligands [CPh,Cu(NCMe)][PF6] δ 46.4, CPh δ 60.2 ppm; [CΦ-Bu,Cu(NCMe)][PF6] δ 43.3, CΦ-Bu δ 58.2 ppm) which is much less than 49 ppm observed for the dimethyl derivative CMe2. This difference is likely due to the methyl groups at the 5-position of CMe2, which shield the P-apex upon κ1-N3 complexation (Fig. 4).

Next, we turned to tris(pyrazolyl)phosphine CH, because its substituted derivatives are apparently too congested around the phosphorus apex for Cu(i) complexation. Reacting CH and [Cu(NCMe)3][PF6] in a 2 : 1 ratio in CH2Cl2 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 1H and 13C NMR spectra recorded in CD2Cl2 at ambient temperature gave only very broad signals that could not be interpreted, 1H and 13C 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 S11). The 31P NMR spectrum at the same temperature demonstrated the different effects Cu coordination has on both sides of the CH ligand. It displayed two singlets for the complex, and a septet at δ −144.7 ppm (JPP,F = 712 Hz) for the PF6− 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 κ1-N3 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 ([CH]2Cu[PF6]) 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 C3 symmetry (r.m.s. deviation 0.149 Å, see Fig. 5). Its molecular structure confirms κ1-coordination of the three pyrazolyl groups of one CH 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 κ1-coordination of the phosphorus apex of the other CH ligand with a Cu–P bond.
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 \([\text{C}^\text{Me}_2\text{Cu}((\text{PPh}_3)_2)][\text{PF}_6]\), reflecting reduced steric crowding, while the non-bonding Cu⋯P 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 \([\text{C}^\text{H}]_2\text{Cu}[\text{PF}_6]\), repetitively recorded solid state 31P NMR data at 297 K are not. Only one singlet is observed at δ 40.3 ppm for the two phosphorus apices and the 13C NMR spectrum suggests the presence of two sets of signals for the pyrazolyl rings in a 2 : 1 ratio. This may suggest that both \(\text{C}^\text{H}\) ligands are bound to Cu(i) with two pyrazolyl groups, leaving the third one uncoordinated. Density functional calculations at B3PW91/6-31G(d) (LANL2DZ for Cu) showed the \(\text{C}2\) symmetric form of the \([\text{C}^\text{H}]_2\text{Cu}\) cation to be only 2.8 kcal mol\(^{-1}\) less stable than the \(\text{C}3\) isomer (Fig. 6).\(^{50}\) This energy difference may even be less as the \(\text{C}2\) form can be stabilized by π-π stacking in the solid state as has been demonstrated for Ag(i) complexes of tris(pyrazolyl)methane ligands \(\text{B}^{25,26}\). 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 \(\text{k}^2\text{k}^2\text{k}^2\text{N}_3\text{P}\) 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 \(\text{C}^\text{H}\) and its inability to form the substituted analogues \([\text{C}^\text{Me}_2, \text{Ph, t-Bu}]\_2\text{Cu}[\text{PF}_6]\) (x = Me\(_2\), Ph, t-Bu).

**Coordination polymer**

With the promising \([\text{C}^\text{H}]_2\text{Cu}[\text{PF}_6]\) result in hand, we were eager to learn whether a one-dimensional coordination polymer \([\text{C}^\text{H}]\text{Cu}[\text{PF}_6]\)\(_n\) could be formed. The logical step was to attempt equimolar mixing of \(\text{C}^\text{H}\) and \([\text{Cu(NCMe)}_3][\text{PF}_6]\). In \(\text{CH}_2\text{Cl}_2\), this gave a beige suspension from which a solid material was isolated that was insoluble in common NMR solvents like \(\text{CD}_2\text{Cl}_2\) and CDCl\(_3\). Solid state NMR was employed to identify its nature. 31P MAS NMR spectroscopy revealed a slightly asymmetric (due to residual dipolar interactions) quartet at δ 42.0 ppm (\(J_{\text{P,Cu}} = 2250\) Hz) and a septet for the \(\text{Cu}^2\)-anion at δ −145.4 ppm (\(J_{\text{P,F}} = 713\) Hz) (see ESI p. S-33\(^{†}\)). The quartet, due to coupling with the two Cu isotopes (\(I = 3/2\)), clearly indicates \(\text{P–Cu}\) coordination. The chemical shift at δ 42.0 ppm suggests a tridentate N-coordinated \(\text{C}^\text{H}\) ligand, as found for \([\text{C}^\text{H}]_2\text{Cu}[\text{PF}_6]\) in solution (δ 39.0 ppm) and for \([\text{C}^\text{H}\text{Cu}((\text{PPh}_3)_2)][\text{PF}_6]\) 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 \([\text{C}^\text{H}]\text{Cu}[[\text{PF}_6]]_n\) with alternating ligands and Cu(i) centers in which each \(\text{C}^\text{H}\) 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 \([\text{C}^\text{H}]\text{Cu}[\text{PF}_6]\)\(_n\) 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”
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 \(P1\) (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-dimensional 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 \(C^\text{Me2}\) 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 \(\left[\text{Cu}^\text{II}\left(\text{PF}_6\right)\right]_n\) was further supported by ligand exchange experiments to trap monomeric units (Scheme 3). For example, reaction of the
polymer with one equivalent of $\text{C}_\text{H}$ in CH$_2$Cl$_2$ gave a clear solution from which a yellow powder was isolated. This was identified by NMR spectroscopy to be identical to the separately synthesized [[(CH)$_2$Cu][PF$_6$]]$_n$ (vide supra), now with an isolated yield of 81%. Likewise, cleaving the polymeric chain with one equivalent of PPh$_3$ in CH$_2$Cl$_2$ gave a 97% isolated yield of [[Cu(Cu(PPh$_3$))][PF$_6$]]. The $^{31}$P NMR spectrum resembles that of [[Cu(PPh$_3$)][PF$_6$]]vide supra and showed a broad singlet at $\delta$ 7.8 ppm for PPh$_3$ bound to Cu(I) and a sharp singlet at $\delta$ 42.4 ppm for the P-apex of $\text{C}_\text{H}$. The $^1$H NMR spectrum showed a 1:1 stoichiometric ratio for the set of signals for $\text{C}_\text{H}$ and a multiplet for the phenyl hydrogens of PPh$_3$. The $^{31}$P MAS NMR spectrum resembled that recorded in solution, but the Cu(1)-coordinated PPh$_3$ appeared as a quartet at $\delta$ 14.2 ppm ($J_{P$_{\text{Cu}}$,Cu}$ = 1862 Hz), while the P-apex of the $\text{C}_\text{H}$ ligand gives a singlet at $\delta$ 40.6 ppm that resembles its chemical shift of $\delta$ 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 phosphate 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 makes 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-1H-pyrazole, 3-42.4 ppm for the P-apex of pyrazole, $^{52}$Cu(NCMe)$_4$][PF$_6$], $^{53}$ and [Na][BArF$_{24}$]$_n$ 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. $^1$H and $^{13}$C NMR spectra were referenced internally to residual solvent resonances (CDCl$_3$: $^1$H: 7.26 ppm (CHCl$_3$), $^{13}$C{${}^1$H}]: 77.16 ppm; CD$_2$Cl$_2$: $^1$H: 5.32 ppm (CDCHCl$_2$), $^{13}$C{${}^1$H}]: 53.84 ppm; CD$_2$CN: $^1$H: 1.94 ppm (CD$_2$HCN), $^{13}$C{${}^1$H}]: 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 $^1$H NMR spectra were determined after applying line narrowing. Solid-state CP-MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer ($^{13}$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 ($\Xi = 40.480747$ MHz). The given values for $^J_{P,Cu}$ refer to the averaged value of couplings to the two isotopes $^{59,61}$Cu and $^{63}$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)$^{3,9}$** 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 completed, 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 $\text{CH}_2$Cl$_2$ ($19$ mL) at $20$ °C. After removal of the mother liquor, the light yellow crystals were dried in vacuo yielding $\text{C}_\text{H}$ (4.03 g, 17.4 mmol, 42.2%). Mp: 105.5–107.6 °C (lit.$^7$ 104 °C). $^1$H NMR (500.2 MHz, CDCl$_3$): $\delta$ 6.46 (dd, $^J_{P$_{\text{Cu}}$,H,P} = 2.6$ Hz, $^J_{H$_{\text{Cu}}$,H} = 1.6$ Hz, 3H; PzH-4), 7.86 (dd, $^J_{P$_{\text{Cu}}$,H,P} = 0.5$ Hz, $^J_{H$_{\text{Cu}}$,H} = 0.4$ Hz, 3H; PzH-3), 8.00 (dd, $^J_{P$_{\text{Cu}}$,H,P} = 0.5$ Hz, $^J_{H$_{\text{Cu}}$,H} = 0.5$ Hz, 3H; PzH-5). $^{13}$C{${}^1$H} NMR (62.9 MHz, CDCl$_3$): $\delta$ 108.9 (d, $^J_{C$_{\text{C}}$,P} = 1.8$ Hz; PzC-4), 135.7 (d, $^J_{C$_{\text{C}}$,P} = 12.1$ Hz; PzC-5), 145.6 (d, $^J_{C$_{\text{C}}$,P} = 10.3$ Hz; PzC-3). $^{31}$P{${}^1$H}
Tris(3,5-dimethylpyrazolyl)phosphine (C\textsubscript{Me\textsubscript{2}})\textsuperscript{4,9} In a similar procedure as reported for tris(pyrazolyl)phosphine (C\textsubscript{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 and the resulting powder, which was not pure according to\textsuperscript{31P} NMR analysis, was washed with toluene until the washings were colorless. After evaporation of the volatiles, the remaining powder was washed with pentane (10 mL) and dried in vacuo to yield 440 mg of a yellow powder, which was not pure according to \textsuperscript{31P} NMR analysis (small unassigned signals between \(\delta 5–15\) and 35–45). Further purification of C\textsubscript{Me\textsubscript{2}} was not successful. \textsuperscript{1H} NMR (500.2 MHz, CDCl\textsubscript{3}); \(\delta 2.11\) (s, 9H; 5-CH\textsubscript{3}), 2.36 (s, 9H; 5-CH\textsubscript{3}), 6.04 (s, 3H; PzH-4). \textsuperscript{13C} NMR (125.8 MHz, CDCl\textsubscript{3}); \(\delta 13.1\) (s; 3-CH\textsubscript{3}), 14.3 (s; 5-CH\textsubscript{3}), 111.7 (d, \(J_{\text{C,P}} = 4.7\) Hz; PzC-4), 147.2 (d, \(J_{\text{C,P}} = 13.6\) Hz; PzC-3), \textsuperscript{31P} NMR (162.0 MHz, CDCl\textsubscript{3}); \(\delta 40.7\) (s, \(J_{\text{P,Se}} = 872\) Hz).

**Attempted preparation of bis(tris(3,5-dimethylpyrazolyl)-phosphine copper(i) hexafluorophosphate ([C\textsubscript{Me\textsubscript{2}}Cu(NCMe)][PF\textsubscript{6}]), [Cu(MeCN)\textsubscript{3}][PF\textsubscript{6}])** (100 mg, 0.268 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 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\textsubscript{H} and CH\textsubscript{3} (1:0.3) according to \textsuperscript{1H} NMR spectroscopy. Further purification of SeC\textsubscript{H} was not successful. \textsuperscript{1H} NMR (400.1 MHz, CDCl\textsubscript{3}); \(\delta 6.51\) (dd, \(J_{\text{H,Cl}} = 2.8\) Hz, 3\textsubscript{H}, 3\textsubscript{H}, 1.5 Hz, 3\textsubscript{H}, PzH-4), 7.96 (ddd, \(J_{\text{H,Cl}} = 2.1\) Hz, 3\textsubscript{H}, 3\textsubscript{H}, 0.5 Hz, 3\textsubscript{H}, PzH-3), 8.04 (ddd, \(J_{\text{H,Cl}} = 2.8\) Hz, 3\textsubscript{H}, 3\textsubscript{H}, 1.4 Hz, 3\textsubscript{H}, 3\textsubscript{H}, PzH-5). \textsuperscript{13C} NMR (125.8 MHz, CDCl\textsubscript{3}); \(\delta 109.7\) (d, \(J_{\text{C,P}} = 6.9\) Hz; PzC-4), 136.6 (d, \(J_{\text{C,P}} = 13.9\) Hz; PzC-5), 147.4 (d, \(J_{\text{C,P}} = 14.9\) Hz; PzC-3), \textsuperscript{31P} NMR (101.3 MHz, CDCl\textsubscript{3}); \(\delta 37.7\) (s, \(J_{\text{P,Se}} = 1014\) Hz).

Tris(3,5-dimethylpyrazolyl)phosphine selenide (SeC\textsubscript{Me\textsubscript{2}}). C\textsubscript{Me\textsubscript{2}} (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 \textsuperscript{31P} NMR analysis (small unassigned signals between \(\delta 5–15\) and 35–45). Further purification of SeC\textsubscript{Me\textsubscript{2}} was not successful. \textsuperscript{1H} NMR (500.2 MHz, CDCl\textsubscript{3}); \(\delta 2.11\) (s, 9H; 5-CH\textsubscript{3}), 2.36 (s, 9H; 5-CH\textsubscript{3}), 6.04 (s, 3H; PzH-4). \textsuperscript{13C} NMR (125.8 MHz, CDCl\textsubscript{3}); \(\delta 13.1\) (s; 3-CH\textsubscript{3}), 14.3 (s; 5-CH\textsubscript{3}), 111.7 (d, \(J_{\text{C,P}} = 4.7\) Hz; PzC-4), 147.2 (d, \(J_{\text{C,P}} = 13.6\) Hz; PzC-3), \textsuperscript{31P} NMR (162.0 MHz, CDCl\textsubscript{3}); \(\delta 40.7\) (s, \(J_{\text{P,Se}} = 872\) Hz).

**Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(i) hexafluorophosphate ([C\textsubscript{Me\textsubscript{2}}Cu(NCMe)][PF\textsubscript{6}]), [Cu(MeCN)\textsubscript{3}][PF\textsubscript{6}])** (505 mg, 1.60 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) was added to a Schlenk vessel containing [Cu(NCMe)\textsubscript{3}][PF\textsubscript{6}] (596 mg, 1.60 mmol). The resulting turbid colorless mixture was stirred overnight followed by cannula filtration. The residue was washed with CH\textsubscript{2}Cl\textsubscript{2} (2 × 3 mL), yielding a colorless solid. All remaining volatiles were removed in vacuo and [C\textsubscript{Me\textsubscript{2}}Cu(NCMe)][PF\textsubscript{6}] (612 mg, 1.08 mmol, 67.7%) remained. \textsuperscript{1H} NMR (500.2 MHz, CD\textsubscript{3}CN); \(\delta 2.31\) (s, 9H; 5-CH\textsubscript{3}), 2.53 (dd, \(J_{\text{H,Cl}} = 1.5\) Hz, 3\textsubscript{H}, 1.0 Hz, 9H; 3-CH\textsubscript{3}), 6.09 (d, \(J_{\text{H,Cl}} = 5.2\) Hz, 3\textsubscript{H}; PzH-4); signals of the coordinated MeCN ligand were not observed due to exchange with the solvent. \textsuperscript{13C} NMR (125.8 MHz, CD\textsubscript{2}CN); \(\delta 12.5\) (d, \(J_{\text{C,P}} = 19.1\) Hz; 5-CH\textsubscript{3}), 13.9 (s; 3-CH\textsubscript{3}), 109.0 (d, \(J_{\text{C,P}} = 4.3\) Hz; PzC-4), 150.5 (d, \(J_{\text{C,P}} = 31.2\) Hz; PzC-5), 156.4 (d, \(J_{\text{C,P}} = 1.6\) 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$_2$CN): $\delta$ = 73.0 (d, $J_{F,P}$ = 36.8 Hz; Ar). $^{31}$P NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta$ = −0.048 mmol (57%). Mp: 281.6 °C (dec). $^1$H NMR (250.1 MHz, CDCl$_3$): δ = 144.7 (p, $J_{C,P}$ = 19.6 Hz; 5-C$_{MeCN}$). 13C{1H} NMR (62.9 MHz, CDCl$_3$): δ = 36.8 Hz; 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$_2$CN): δ = −72.9 (d, $J_{F,P}$ = 171 Hz; P$_{PF6}$). $^{31}$P NMR (162.0 MHz, CDCl$_3$ + CD$_2$CN): δ = −144.5 (sept, $J_{J,C,P}$ = 171 Hz; P$_{PF6}$), 45.4 (s; P[PF$_6$]). HR-ESI-MS: calec for C$_{25}$H$_{21}$Cu$_2$N$_6$P$_3$ 523.0856, found 523.0835.

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(i) hexafluorophosphate ([C$_{Bu}^+$Cu(NCMe)$_3$][PF$_6$]). C$_{Bu}^+$Cu$_2$ (0.50 g, 1.13 mmol) and [Cu(NCMe)$_3$][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$_{Bu}^+$Cu(NCMe)$_3$][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).

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(i) hexafluorophosphate ([C$_{Bu}^+$Cu(NCMe)$_3$][PF$_6$]). C$_{Bu}^+$Cu$_2$ (0.50 g, 1.13 mmol) and [Cu(NCMe)$_3$][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$_{Bu}^+$Cu(NCMe)$_3$][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).

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(i) hexafluorophosphate ([C$_{Bu}^+$Cu(NCMe)$_3$][PF$_6$]). C$_{Bu}^+$Cu$_2$ (0.50 g, 1.13 mmol) and [Cu(NCMe)$_3$][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$_{Bu}^+$Cu(NCMe)$_3$][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).

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(i) hexafluorophosphate ([C$_{Bu}^+$Cu(NCMe)$_3$][PF$_6$]). C$_{Bu}^+$Cu$_2$ (0.50 g, 1.13 mmol) and [Cu(NCMe)$_3$][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$_{Bu}^+$Cu(NCMe)$_3$][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).
(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$_2$Cl$_2$): δ 6.54 (ddd, $^3$J$_{HH}=3.4$ Hz, $^3$J$_{HP}=2.8$ Hz, $^3$J$_{PF}=1.9$ Hz, 3H; Pz$_{4}$CD$_2$Cl$_2$), 6.63 (ddd, $^3$J$_{HH}=2.8$ Hz, $^3$J$_{HP}=1.6$ Hz, 3H; Pz$_{4}$CD$_2$H), 7.64 (dd, $^3$J$_{HH}=2.8$ Hz, 3H; Pz$_{4}$CD$_2$H), 8.05 (m, $^3$J$_{HH}=1.5$ Hz, 3H; Pz$_{4}$CD$_2$-3), 110.2 (s, $^3$J$_{CP}=6.7$ Hz; Pz$_{4}$CD$_2$-3), 138.8 (d, $^3$J$_{CP}=38.0$ Hz; Pz$_{4}$CD$_2$-3), 146.7 (d, $^3$J$_{CP}=14.5$ Hz; Pz$_{4}$CD$_2$-3).

Tri[pyrazolyl]phosphine copper(I) hexafluorophosphate ([Cu(C$_3$P$_3$)Cl]PF$_6$). CH$_2$Cl$_2$ (50 mL) was added to a mixture of [Cu(NCMe)$_2$][PF$_6$] (1.86 g, 5.00 mmol) and Cu$_2$ (1.18 g, 1.00 mmol) to obtain a clear colorless solution, which appeared to be cracked into two fragments. Consequently, two attempts were made with no restraints.

X-ray crystal structure determination

A table containing the experimental details of the crystal structure determination is included in the ESI (ESI S.67).

**[CuMe$_2$Cl]PF$_6$.** $^{3}P$ NMR (235.3 MHz, CDCl$_3$): δ −71.8 (d, $^3$J$_{PF}=713$ Hz; PF$_6$), $^{31}$P($^1$H) NMR (162.0 MHz, 201 K, CD$_2$Cl$_2$): δ −144.7 (sept, $^3$J$_{PF}=713$ Hz; PF$_6$), 40.3 (s; P(Pz$_3$)). HR-ESI-MS: calcd for [C$_5$H$_4$Cu$_2$N$_3$P$_2$]$:^{31}$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$^{+}$].
0.91 mm$^{-1}$. 102481 reflections were measured on a Nonius KappaCCD diffractometer with a rotating anode and a graphite monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65$ Å$^{-1}$. X-ray intensities were integrated with the Denzo software. Multiscan absorption correction and scaling were performed with SADABS (correction range 0.54–0.89). 17382 reflections were unique ($R_{\text{int}} = 0.067$), of which 12960 were observed ($I > 2\sigma(I)$). The structure was solved with automated Patterson methods using the program DIRDIF-08. Least-squares refinement was performed with SHELXL-2014 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). $R_f$/wR$_2$ $[I > 2\sigma(f)]$: 0.0481/0.1134. $R_f$/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.

$\left\{[\text{C}^{16}\text{Cu}[\text{PF}_6]]_{\text{x}}\right\}$3C$_2$H$_4$Cl$_2$. [C$_{16}$H$_{18}$CuN$_{12}$P$_2$][PF$_6$]·3C$_2$H$_4$Cl$_2$, $F_w = 672.89$,35 colorless needle, 0.41 × 0.17 × 0.15 mm$^3$, trigonal, P31c (no. 159), $a = b = 19.5288(14)$ Å, $c = 18.0311(14)$ Å, $V = 5955.3(10)$ Å$^3$, $Z = 8$, $D_x = 1.501$ g cm$^{-3}$, $\mu = 0.96$ mm$^{-1}$. 83 520 reflections were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator ($\lambda = 0.71073$ Å) at a temperature of 110(2) K up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65$ Å$^{-1}$. X-ray intensities were integrated with the Eval15 software. Numerical absorption correction and scaling were performed with SADABS (correction range 0.61–0.94). 6330 reflections were unique ($R_{\text{int}} = 0.048$), of which 5148 were observed ($I > 2\sigma(I)$). The structure was solved with Patterson superposition methods using the program SHELXL. Least-squares refinement was performed with SHELXL-2014 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). $R_f$/wR$_2$ $[I > 2\sigma(f)]$: 0.0462/0.1100. $R_f$/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-modelled disorder). Geometry calculations and checking for higher symmetry were performed with the PLATON program.

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