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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 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][PF₆] 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.

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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

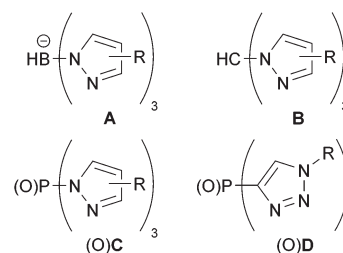


Fig. 1 Scorpion-type ligands.

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-

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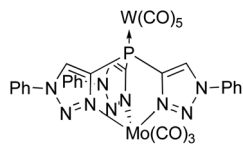


Fig. 2 A bimetallic complex supported by ligand D.

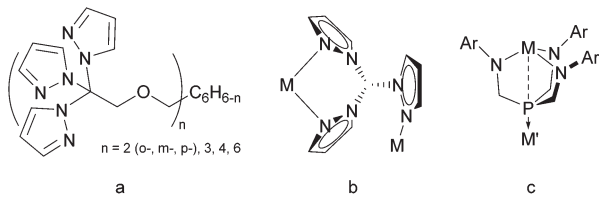


Fig. 3 (a) Multitopic tris(pyrazolyl)methane ligands, (b) the κ^2 - κ^1 bonding mode, and (c) a bimetallic Janus-type complex.

(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.

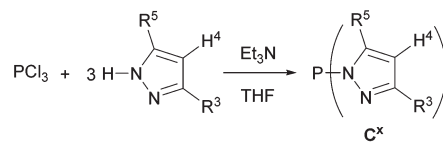
Besides multimetallic complexes, scorpion ligands **B** also enable access to coordination macrocycles and polymers as shown in the seminal work of Reger,²⁴ who used tethered, multitopic tris(pyrazolyl) moieties (Fig. 3a) with silver(i) complexes to generate an abundance of well-identified supramolecular 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 $A^{(t-Bu/Ph,4-CN)}$ 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(mercaptiothiadiazolyl)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 polymers⁴¹ 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 C^H and tris(dimethylpyrazolyl)phosphine C^{Me_2} ,^{8,9} and the new, more congested tris(3-phenylpyrazolyl)phosphine C^{Ph} and tris(3-tert-butylpyr-

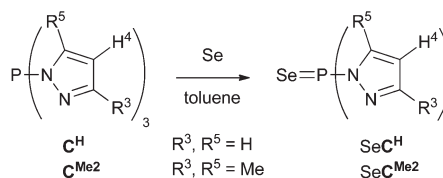


	C^H	C^{Me_2}	C^{Ph}	C^{t-Bu}
$R^3 =$	H	Me	Ph	<i>t</i> -Bu
$R^5 =$	H	Me	H	H
Yield (%):	42	96	52	81

Scheme 1 Synthesis of tris(pyrazolyl)phosphines C^H - C^{t-Bu} .

azolyl)phosphine C^{t-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 C^H and C^{Me_2} or under reflux for the bulkier C^{Ph} and C^{t-Bu} . The reaction progress was monitored by ³¹P NMR spectroscopy using the characteristic singlet for the phosphorus apex of the products (δ 61.1 (C^H), 72.0 (C^{Me_2}), 60.2 (C^{Ph}), and 58.2 (C^{t-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 C^H (recrystallization) and C^{Ph} (washings), reducing their isolated yields significantly. The ¹H and ¹³C NMR spectra revealed simple signal patterns, reflecting the expected equivalence of the three pyrazolyl groups; the ¹³C{¹H} NMR spectra showed the characteristic doublets ($J_{C,P} \sim 10$ Hz) for the C³ and C⁵ 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 C^X , we have investigated selenides SeC^H and SeC^{Me_2} (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 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 SeC^{Me_2} (~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 SeC^H and SeC^{Me_2} .



for selenophosphoramides, indicating C^{Me_2} 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^{Me_2} is also reflected by the harsh conditions required for the formation of their selenides.

Complexation to copper(I)

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^{Me_2} 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(I)-complex with C would result from simply treating a Cu(I) 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^{Me_2} .

A colorless solid precipitated, yielding crystals suitable for X-ray diffraction upon recrystallization (CH_2Cl_2 /pentane). The determined molecular structure reveals $[C^{Me_2}Cu(NCMe)][PF_6]$ (Fig. 4, left), which must have been formed by replacing three acetonitrile ligands of $[Cu(NCMe)_4][PF_6]$ for one C^{Me_2} . Apparently, the phosphorus apex of the second C^{Me_2} is unable to replace the remaining acetonitrile. Reacting C^{Me_2} 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^{Me_2} 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(I)-complexes.⁴⁹ The 1H 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_3CN 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 $[C^{Me_2}Cu(NCMe)][PF_6]$, $\Delta J_{C3,P} = -8.5$, $\Delta J_{C4,P} = 4.3$, 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-

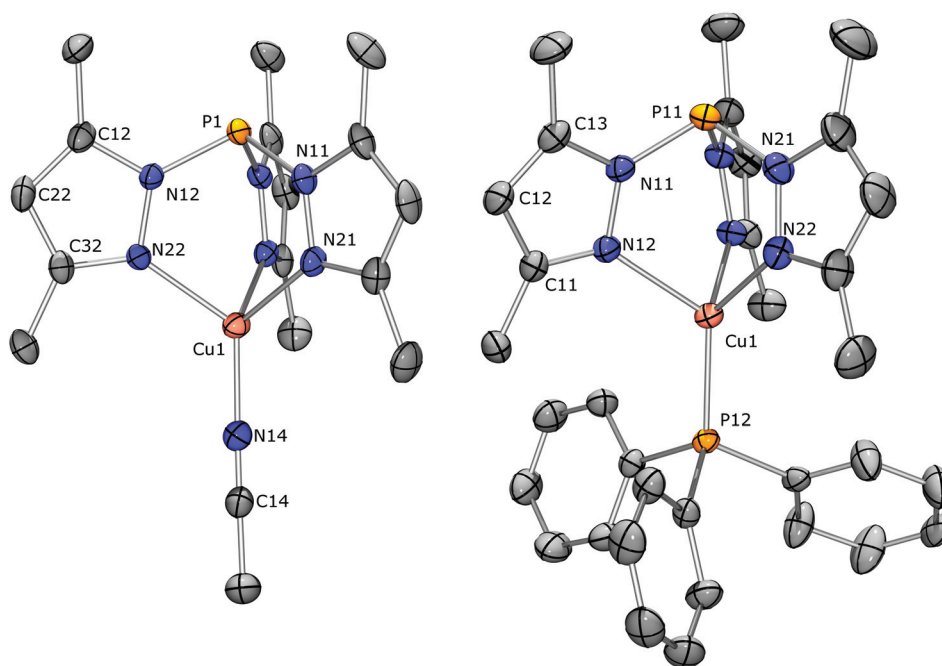


Fig. 4 Displacement ellipsoid plot of $[C^{Me_2}Cu(NCMe)][PF_6]$ (left) and $[C^{Me_2}Cu(PPh_3)][PF_6]$ (right) drawn at the 50% probability level. The PF_6 anions and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for $[C^{Me_2}Cu(NCMe)][PF_6]$: Cu1–N21 2.077(3), Cu1–N14 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 $[C^{Me_2}Cu(PPh_3)][PF_6]$, without PF_6 anions and CH_2Cl_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).



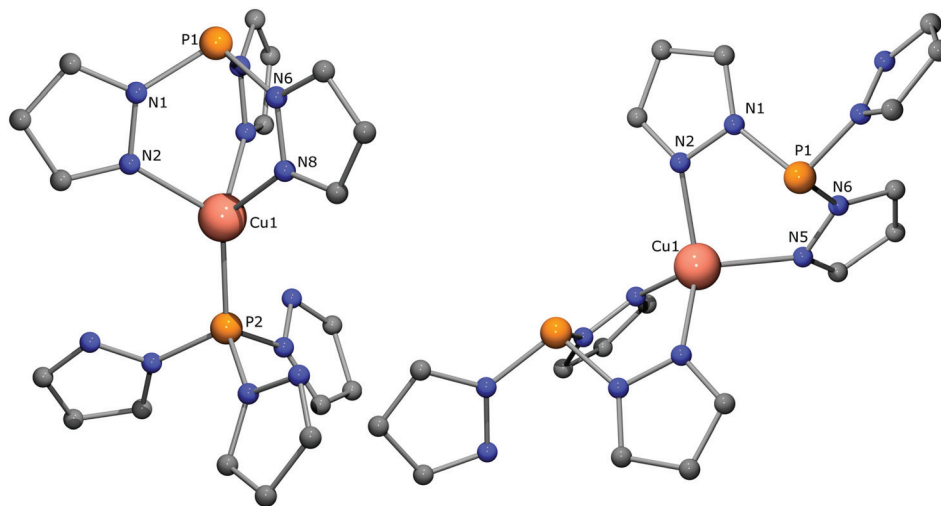


Fig. 6 Optimized structures for the $\kappa^3, \kappa^1\text{-N}_3\text{P}$ (left) and $\kappa^2, \kappa^2\text{-N}_4$ (right) bound isomers of $[(\text{C}^{\text{H}})_2\text{Cu}]^+$ as calculated at the B3PW91/6-31G(d) (LANL2DZ for Cu) level of theory. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for $\kappa^3, \kappa^1\text{-N}_3\text{P}$: 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 $\kappa^2, \kappa^2\text{-N}_4$: 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 $[\text{C}^{\text{Me}2}\text{Cu}(\text{PPh}_3)][\text{PF}_6]$, 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 $[(\text{C}^{\text{H}})_2\text{Cu}][\text{PF}_6]$, 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(I) 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 $[(\text{C}^{\text{H}})_2\text{Cu}]$ 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(I) 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 $\kappa^3, \kappa^1\text{-N}_3\text{P}$ 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

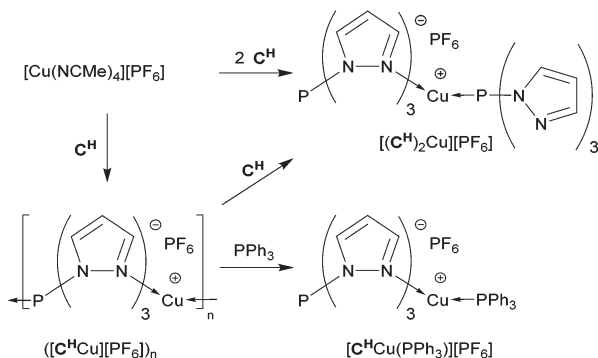
concur with the low P-donor ability of C^{H} and its inability to form the substituted analogues $[(\text{C}^{\text{X}})_2\text{Cu}][\text{PF}_6]$ ($\text{X} = \text{Me}_2, \text{Ph}, t\text{-Bu}$).

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 C^{H} and $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$. In CH_2Cl_2 , this gave a beige suspension from which a solid material was isolated that was insoluble in common NMR solvents like CD_2Cl_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 ($^1J_{\text{P,Cu}} = 2250$ Hz) and a septet for the PF_6^- anion at δ –145.4 ppm ($^1J_{\text{P,F}} = 713$ Hz) (see ESI p. S-33†). The quartet, due to coupling with the two Cu isotopes ($I = 3/2$), clearly indicates P–Cu coordination. The chemical shift at δ 42.0 ppm suggests a tridentate N-coordinated C^{H} ligand, as found for $[(\text{C}^{\text{H}})_2\text{Cu}][\text{PF}_6]$ in solution (δ 39.0 ppm) and for $[\text{C}^{\text{H}}\text{Cu}(\text{PPh}_3)][\text{PF}_6]$ 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 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 $[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$ 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”





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 $[C^H)Cu(PPh_3)][PF_6]$. The ^{31}P NMR spectrum resembles that of $[C^{Me_2}Cu(PPh_3)][PF_6]$ (*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 ($J_{P,63Cu} = 1862$ 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-1H-pyrazole,⁵² 3-*tert*-butyl-1H-pyrazole,⁵² $[Cu(NCMe)_4][PF_6]$,⁵³ and $[Na][BArF_2]$ 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_2Cl_2 : 1H : 5.32 ppm ($CDHCl_2$), $^{13}C\{^1H\}$: 53.84 ppm; CD_3CN : 1H : 1.94 ppm (CD_2HCN), $^{13}C\{^1H\}$: 1.32 ppm). Other nuclei were referenced to external standards: ^{19}F : $BF_3 \cdot Et_2O$ (0.0 ppm) and ^{31}P : 85% H_3PO_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_3PO_4 as the external standard ($\mathcal{E} = 40.480747$ 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 ($Et_3N \cdot HCl$) 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_2Cl_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; PzH-4), 7.86 (ddd, $^3J_{H,H} = 1.6$ Hz, $^4J_{H,H} = 0.5$ Hz, $^4J_{H,P} = 0.4$ Hz, 3H; PzH-3), 8.00 (ddd, $^3J_{H,H} = 2.6$ Hz, $^3J_{H,P} = 1.7$ Hz, $^4J_{H,H} = 0.5$ Hz, 3H; PzH-5). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 108.9 (d, $^3J_{C,P} = 1.8$ Hz; PzC-4), 135.7 (d, $^2J_{C,P} = 12.1$ Hz; PzC-5), 145.6 (d, $^3J_{C,P} = 10.3$ Hz; PzC-3). $^{31}P\{^1H\}$



coordinated MeCN ligand were not observed due to exchange with the solvent. ^{19}F NMR (235.3 MHz, CD_3CN): δ -73.0 (d, $^1J_{\text{F,P}} = 706.0$ Hz; PF_6). ^{31}P NMR (162.0 MHz, CD_3CN): δ -144.6 (sept, $^1J_{\text{P,F}} = 706.3$ Hz; PF_6), 23.3 (s; P(Pz)). $^{31}\text{P}\{^1\text{H}\}$ CP/MAS NMR (162.0 MHz): δ -144.1 (sept, $^1J_{\text{P,F}} = 710$ Hz; PF_6), 21.4 (s; P(Pz)).

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(i) tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate ($[\text{C}^{\text{Me}_2}\text{Cu}(\text{NCMe})][\text{BARF}_{24}]$). $[\text{C}^{\text{Me}_2}\text{Cu}(\text{NCMe})][\text{PF}_6]$ (48 mg, 0.085 mmol), $[\text{Na}][\text{BARF}_{24}]$ (75 mg, 0.085 mmol) and CH_2Cl_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 $[\text{C}^{\text{Me}_2}\text{Cu}(\text{NCMe})][\text{BARF}_{24}]$ as a colorless solid (62 mg, 0.048 mmol, 57%). Mp: 151.7–152.6 °C. ^1H 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, $^4J_{\text{H,P}} = 5.3$ Hz, 3H; PzH-4), 7.51 (s, 4H; *p*-ArH), 7.71 (s, 8H; *o*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3): δ 2.7 (s; NCCH_3), 12.1 (d, $^3J_{\text{C,P}} = 19.6$ Hz; 5- CH_3), 13.8 (s; 3- CH_3), 108.8 (d, $^3J_{\text{C,P}} = 4.5$ Hz; PzC-4), 115.3 (s; NCCH_3), 117.6 (m, $^3J_{\text{C,F}} = 3.8$ Hz; *p*-ArC), 124.7 (q, $^1J_{\text{C,F}} = 272.5$ Hz; CF_3), 129.1 (q, $^2J_{\text{C,F}} = 32$ Hz; *m*-ArC), 135.0 (s; *o*-ArC), 147.9 (d, $^2J_{\text{C,P}} = 31.4$ Hz; PzC-5), 155.7 (d, $^3J_{\text{C,P}} = 1.9$ Hz; PzC-3), 161.9 (q, $^1J_{\text{C,B}} = 49.9$ 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 $\text{C}_{15}\text{H}_{21}\text{CuN}_6\text{P}$ (M-MeCN-B($\text{C}_6\text{H}_3(\text{CF}_3)_2$) $_4$) 379.0856, found 379.0815.

Tris(3,5-dimethylpyrazolyl)phosphine triphenylphosphine copper(i) hexafluorophosphate ($[\text{C}^{\text{Me}_2}\text{Cu}(\text{PPh}_3)][\text{PF}_6]$). A Schlenk vessel was charged with $[\text{C}^{\text{Me}_2}\text{Cu}(\text{NCMe})][\text{PF}_6]$ (95.9 mg, 0.169 mmol) and triphenylphosphine (44.3 mg, 0.169 mmol). CH_2Cl_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 $[\text{C}^{\text{Me}_2}\text{Cu}(\text{PPh}_3)][\text{PF}_6]$ (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 $[\text{C}^{\text{Me}_2}\text{Cu}(\text{PPh}_3)][\text{PF}_6]$ in CH_2Cl_2 . After allowing slow diffusion of the pentane for four days, colorless crystals had formed. Mp: 281.6 °C (dec). ^1H NMR (250.1 MHz, CDCl_3): δ 1.76 (s, 9H; 3- CH_3), 2.63 (s, 9H; 5- CH_3), 6.05 (d, $^4J_{\text{H,P}} = 5.4$ Hz, 3H; PzH-4), 7.36–7.60 (m, 15H; PhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3): δ 12.4 (d, $^3J_{\text{C,P}} = 20.5$ Hz; 5- CH_3), 14.3 (s; 3- CH_3), 109.5 (d, $^3J_{\text{C,P}} = 4.4$ Hz; PzC-4), 129.3 (d, $^3J_{\text{C,P}} = 10.0$ Hz; *m*-PhC), 130.9 (d, $^4J_{\text{C,P}} = 1.7$ Hz; *p*-PhC), 132.8 (d, $^1J_{\text{C,P}} = 36.8$ Hz; *ipso*-PhC), 134.0 (d, $^2J_{\text{C,P}} = 15.5$ Hz; *o*-PhC), 149.2 (d, $^2J_{\text{C,P}} = 32.3$ Hz; PzC-5), 156.7 (d, $^3J_{\text{C,P}} = 1.3$ Hz; PzC-3). ^{19}F NMR (235.3 MHz, CDCl_3): δ -73.7 (d, $^1J_{\text{F,P}} = 712$ Hz; PF_6). ^{31}P NMR (101.3 MHz, CDCl_3): δ -144.3 (sept, $^1J_{\text{P,F}} = 712$ Hz; PF_6), 6.5 (br. s; P(Ph) $_3$), 21.4 (s; P(Pz) $_3$). HR-ESI-MS: calcd for $\text{C}_{33}\text{H}_{36}\text{CuN}_6\text{P}_2$ (M- PF_6) 641.1767, found 641.1698.

Acetonitrile tris(3-phenylpyrazolyl)phosphine copper(i) hexafluorophosphate ($[\text{C}^{\text{Ph}}\text{Cu}(\text{NCMe})][\text{PF}_6]$). C^{Ph} (0.50 g, 1.1 mmol) and $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ (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*, $[\text{C}^{\text{Ph}}\text{Cu}(\text{NCMe})][\text{PF}_6]$ (0.43 g, 0.55 mmol, 51%) was collected as a pale yellow powder, retaining 1 eq. of THF according to ^1H NMR spectroscopy. Mp: 225–226 °C (dec). ^1H NMR (500.2 MHz, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): 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. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ 107.4 (d, $^3J_{\text{C,P}} = 8.1$ 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, $^2J_{\text{C,P}} = 26.8$ 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, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ -72.9 (d, $^1J_{\text{F,P}} = 710$ Hz; PF_6). ^{31}P -NMR (162.0 MHz, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ -144.5 (sept, $^1J_{\text{P,F}} = 711$ Hz; PF_6), 46.4 (s; P(Pz)). HR-ESI-MS: calcd for $\text{C}_{27}\text{H}_{21}\text{CuN}_6\text{P}$ (M-MeCN- PF_6) 523.0856, found 523.0835.

Acetonitrile tris(3-*tert*-butylpyrazolyl)phosphine copper(i) hexafluorophosphate ($[\text{C}^{\text{t-Bu}}\text{Cu}(\text{NCMe})][\text{PF}_6]$). $\text{C}^{\text{t-Bu}}$ (0.50 g, 1.3 mmol) and $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ (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*, $[\text{C}^{\text{t-Bu}}\text{Cu}(\text{NCMe})][\text{PF}_6]$ (0.35 g, 0.48 mmol, 39%) was collected as a pale yellow powder, retaining 1 eq. of THF according to ^1H NMR spectroscopy. Mp: 165–167 °C (dec). ^1H -NMR (500.2 MHz, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ 1.35 (s, 27H; $\text{C}(\text{CH}_3)_3$), 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, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ 29.6 (s; $\text{C}(\text{CH}_3)_3$), 32.3 (s; $\text{C}(\text{CH}_3)_3$), 106.1 (d, $^3J_{\text{C,P}} = 10.0$ Hz; PzC-4), 138.2 (d, $^2J_{\text{C,P}} = 40.3$ 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, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ -73.0 (d, $^1J_{\text{F,P}} = 711$ Hz; PF_6). ^{31}P -NMR (162.0 MHz, $\text{CDCl}_3 + \text{CD}_3\text{CN}$): δ -144.5 (sept, $^1J_{\text{P,F}} = 711$ Hz; PF_6), 43.3 (s; P(Pz)). HR-ESI-MS: calcd for $\text{C}_{21}\text{H}_{33}\text{CuN}_6\text{P}$ (M-MeCN- PF_6) 463.1795, found 463.1784.

Bis(tris(pyrazolyl)phosphine)copper(i) hexafluorophosphate ($[(\text{C}^{\text{H}})_2\text{Cu}][\text{PF}_6]$). *Procedure A* starting with $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$: CH_2Cl_2 (30 mL) was added to a mixture of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ (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_2O (10 mL) and dried *in vacuo* to yield $[(\text{C}^{\text{H}})_2\text{Cu}][\text{PF}_6]$ (0.294 mg, 0.437 mmol, 88.0%). *Procedure B* starting with $[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$: CH_2Cl_2 (10 mL) was added to a mixture of $[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$ (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 $[(\text{C}^{\text{H}})_2\text{Cu}][\text{PF}_6]$ (0.26 g, 0.386 mmol, 80.8%). 0.14 g of this material was dissolved in CH_2Cl_2



(10 mL). The resulting pale solution was filtered and concentrated to one third of its volume. Storing this solution at $-20\text{ }^{\circ}\text{C}$ resulted in a small amount of crystals, suitable for an X-ray diffraction study. Mp: 199.8–201.4 $^{\circ}\text{C}$ (dec). ^1H NMR (400.1 MHz, 201 K, CD_2Cl_2): δ 6.54 (ddd, $^4J_{\text{H,P}} = 3.4\text{ Hz}$, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, $^3J_{\text{H,H}} = 1.9\text{ Hz}$, 3H; $\text{Pz}_{\text{K3N}}\text{H-4}$), 6.63 (dd, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, $^3J_{\text{H,H}} = 1.6\text{ Hz}$, 3H; $\text{Pz}_{\text{K1P}}\text{H-4}$), 7.64 (d, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, 3H; $\text{Pz}_{\text{K1P}}\text{H-5}$), 8.05 (m, $^3J_{\text{H,H}} = 1.5\text{ Hz}$, 3H; $\text{Pz}_{\text{K1P}}\text{H-3}$), 8.28 (dd, $^3J_{\text{H,P}} = 4.8\text{ Hz}$, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, 3H; $\text{Pz}_{\text{K3N}}\text{H-5}$) 8.41 (ddd, $^3J_{\text{H,H}} = 1.9\text{ Hz}$, $^4J_{\text{H,P}} = 1.3\text{ Hz}$, $^4J_{\text{H,H}} = 0.5\text{ Hz}$, 3H; $\text{Pz}_{\text{K3N}}\text{H-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, 201 K, CD_2Cl_2): δ 108.4 (d, $^2J_{\text{C,P}} = 8.7\text{ Hz}$; $\text{Pz}_{\text{K3N}}\text{C-4}$), 110.2 (s, $\text{Pz}_{\text{K1P}}\text{C-4}$), 134.4 (d, $^2J_{\text{C,P}} = 6.7\text{ Hz}$; $\text{Pz}_{\text{K1P}}\text{C-5}$), 138.8 (d, $^2J_{\text{C,P}} = 38.0\text{ Hz}$; $\text{Pz}_{\text{K3N}}\text{C-5}$), 146.7 (d, $^3J_{\text{C,P}} = 14.5\text{ Hz}$; $\text{Pz}_{\text{K1P}}\text{C-3}$), 148.0 (s; $\text{Pz}_{\text{K3N}}\text{C-3}$). ^{19}F NMR (235.3 MHz, CDCl_3): δ -71.8 (d, $^1J_{\text{P,F}} = 713\text{ Hz}$; PF_6). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, 201 K, CD_2Cl_2): δ -144.7 (sept, $^1J_{\text{P,F}} = 712\text{ Hz}$; PF_6), 39.0 (s; $\text{P}(\text{Pz}_{\text{K3N}})$), 62.0 (br.s; $\text{P}(\text{Pz}_{\text{K1P}})$). $^{31}\text{P}\{^1\text{H}\}$ CP/MAS NMR (162.0 MHz): δ -143.4 (sept, $^1J_{\text{P,F}} = 713\text{ Hz}$; PF_6), 40.3 (s; $\text{P}(\text{Pz})$). HR-ESI-MS: calcd for $\text{C}_{18}\text{H}_{18}\text{CuN}_{12}\text{P}_2$ ($(\text{C}^{\text{H}})_2\text{Cu}^+$) 527.0543, found 527.0530 m/z (%) 295 (100) $[\text{M}-\text{P}(\text{Pz})_3]^+$, 330 (21.4), 362 (3.6), 476 (20.5), 492 (9.5), 527 (22.6) $[\text{M}]^+$.

Tris(pyrazolyl)phosphine copper(i) hexafluorophosphate ($[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$). CH_2Cl_2 (50 mL) was added to a mixture of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ (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 ($4 \times 10\text{ mL}$) and subsequently dried *in vacuo* affording $[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$ (2.00 g, 4.53 mmol, 91%). Mp: 196.0–197.4 $^{\circ}\text{C}$ (dec). $^{31}\text{P}\{^1\text{H}\}$ MAS NMR (162.0 MHz): δ -145.4 (sept, $^1J_{\text{P,F}} = 713\text{ Hz}$; PF_6), 42.0 (q, $^1J(\text{P,Cu}) = 2250\text{ Hz}$; $\text{P}(\text{Pz})$). Anal. Calcd for $\text{C}_9\text{H}_9\text{CuF}_6\text{N}_6\text{P}_2$: 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 $[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$ resulted in a clear colorless solution, which allowed the following NMR spectra to be recorded. ^1H NMR (400.1 MHz, CD_3CN): δ 6.61 (ddd, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, $^4J_{\text{H,P}} = 2.2\text{ Hz}$, $^3J_{\text{H,H}} = 1.7\text{ Hz}$, 3H; PzH-4), 8.15 (d, $^3J_{\text{H,H}} = 1.7\text{ Hz}$, 3H; PzH-3), 8.18 (dd, $^3J_{\text{H,P}} = 3.7\text{ Hz}$, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, 3H; PzH-5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_3CN): δ 110.1 (d, $^3J_{\text{C,P}} = 6.2\text{ Hz}$; PzC-4), 139.3 (d, $^2J_{\text{C,P}} = 24.2\text{ Hz}$; PzC-5), 148.6 (d, $^3J_{\text{C,P}} = 5.2\text{ Hz}$; PzC-3). ^{19}F NMR (235.3 MHz, CD_3CN): δ -72.8 (d, $^1J_{\text{P,F}} = 713\text{ Hz}$; PF_6). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CD_3CN): δ -144.6 (sept, $^1J_{\text{P,F}} = 707\text{ Hz}$; PF_6), 47.4 (br.s; $\text{P}(\text{Pz})$). 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 $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ in dichloroethane; the crystals grew at the interface between the two layers as fine needles.

Triphenylphosphine tris(pyrazolyl)phosphine copper(i) hexafluorophosphate ($[(\text{C}^{\text{H}}\text{Cu}(\text{PPh}_3))][\text{PF}_6]$). CH_2Cl_2 (20 mL) was added to a mixture of $[(\text{C}^{\text{H}}\text{Cu}][\text{PF}_6])_n$ (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 $[(\text{C}^{\text{H}}\text{Cu}(\text{PPh}_3))][\text{PF}_6]$ (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 $[(\text{C}^{\text{H}}\text{Cu}(\text{PPh}_3))][\text{PF}_6]$. Mp: 205.6–208.8 $^{\circ}\text{C}$ (dec). ^1H NMR (500.2 MHz, CDCl_3): δ 6.44 (ddd, $^4J_{\text{H,P}} = 3.2\text{ Hz}$, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, $^3J_{\text{H,H}} = 1.9\text{ Hz}$, 3H; PzH-4), 7.44 (ddd, $^3J_{\text{H,H}} = 1.9\text{ Hz}$, $^4J_{\text{H,P}} = 1.4\text{ Hz}$, $^4J_{\text{H,H}} = 0.5\text{ Hz}$ overlapping; PzH-5), 7.42–7.55 (m, overlapping, 15H; PhH), 8.37 (ddd, $^3J_{\text{H,P}} = 5.2\text{ Hz}$, $^3J_{\text{H,H}} = 2.8\text{ Hz}$, $^4J_{\text{H,H}} = 0.5\text{ Hz}$, 3H; PzH-3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 108.7 (d, $^3J_{\text{C,P}} = 8.9\text{ Hz}$; PzC-4), 129.4 (d, $^3J_{\text{C,P}} = 10.1\text{ Hz}$; *m*-PhC), 130.9 (s; *p*-PhC), 132.6 (d, $^1J_{\text{C,P}} = 38.0\text{ Hz}$; *ipso*-PhC), 133.6 (d, $^2J_{\text{C,P}} = 16.0\text{ Hz}$; *o*-PhC), 139.3 (d, $^2J_{\text{C,P}} = 39.2\text{ Hz}$; PzC-5), 146.9 (s; PzC-3). ^{19}F NMR (235.3 MHz, CDCl_3): δ -72.0 (d, $^1J_{\text{P,F}} = 713\text{ Hz}$; PF_6). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3): δ -144.1 (sept, $^1J_{\text{P,F}} = 713\text{ Hz}$; PF_6), 7.8 (s; $\text{P}(\text{Ph})$), 42.4 (s; $\text{P}(\text{Pz})$). $^{31}\text{P}\{^1\text{H}\}$ CP/MAS NMR (162.0 MHz): δ -143.4 (sept, $^1J_{\text{P,F}} = 712\text{ Hz}$; PF_6), 14.2 (q, $^1J(\text{P}, ^{63}\text{Cu}) = 1862\text{ Hz}$; $\text{P}(\text{Ph})$), 40.6 (s; $\text{P}(\text{Pz})$). HR-ESI-MS: calcd for $\text{C}_{27}\text{H}_{24}\text{CuN}_6\text{P}_2$ ($\text{C}^{\text{H}}\text{Cu}(\text{PPh}_3)^+$) 557.0828, found 557.0839; m/z (%) 366 (75) $[\text{Ph}_3\text{PCuNCMe}]^+$, 557 (61) $[\text{M}]^+$, 587 (100) $[(\text{Ph}_3\text{P})_2\text{Cu}]^+$.

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[†]).

$[\text{C}^{\text{Me2}}\text{Cu}(\text{NCMe})][\text{PF}_6]$. $[\text{C}_{17}\text{H}_{24}\text{CuN}_7\text{P}](\text{PF}_6)$, $F_w = 565.91$, colorless needle, $0.41 \times 0.14 \times 0.06\text{ mm}^3$, monoclinic, $C2/c$ (no. 15), $a = 26.0651(16)$, $b = 7.7824(3)$, $c = 25.9327(13)\text{ \AA}$, $\beta = 116.124(3)^\circ$, $V = 4723.0(4)\text{ \AA}^3$, $Z = 8$, $D_x = 1.592\text{ g cm}^{-3}$, $\mu = 1.13\text{ mm}^{-1}$. 33686 reflections were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator ($\lambda = 0.71073\text{ \AA}$) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65\text{ \AA}^{-1}$. 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 TWINABS⁵⁶ (correction range 0.57–0.75). 5582 reflections were unique ($R_{\text{int}} = 0.057$), 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-2014⁵⁸ 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 \AA^{-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

$[\text{C}^{\text{Me2}}\text{Cu}(\text{PPh}_3)][\text{PF}_6]$. $[\text{C}_{33}\text{H}_{36}\text{CuN}_6\text{P}_2](\text{PF}_6) \cdot \text{CH}_2\text{Cl}_2$, $F_w = 872.05$, colorless block, $0.51 \times 0.36 \times 0.12\text{ mm}^3$, monoclinic, $P2_1/n$ (no. 14), $a = 14.3558(1)$, $b = 31.5939(2)$, $c = 16.7621(1)\text{ \AA}$, $\beta = 90.6316(2)^\circ$, $V = 7602.08(8)\text{ \AA}^3$, $Z = 8$, $D_x = 1.524\text{ g cm}^{-3}$, $\mu =$



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