Supporting Information

Cooperative H₂ Activation on Dicopper(I) Facilitated by Reversible Dearomatization of an “Expanded PNNP Pincer” Ligand

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Author Contributions

D.B. Conceptualization: Lead; Data curation: Lead; Formal analysis: Lead; Funding acquisition: Lead; Investigation: Equal; Methodology: Equal; Project administration: Lead; Resources: Lead; Supervision: Lead; Validation: Lead; Visualization: Lead; Writing - Original Draft: Lead; Writing - Review & Editing: Lead
E.K. Data curation: Supporting; Formal analysis: Lead; Investigation: Equal; Methodology: Equal; Writing - Original Draft: Supporting; Writing - Review & Editing: Supporting
M.L. Data curation: Equal; Formal analysis: Equal; Methodology: Supporting; Writing - Review & Editing: Supporting.
Experimental methods:

**General considerations.** All manipulations were performed under inert atmosphere using standard Schlenk techniques or inside of a N$_2$-filled M. Braun glovebox using anhydrous solvents and reagents, unless noted otherwise. Glassware was dried in vacuum at 150 °C. Solvents were collected from an M. Braun MB-SPS-800 solvent purification system and stored over 4 Å molecular sieves, except for CH$_2$Cl$_2$, where 3 Å molecular sieves were used. Deuterated solvents were obtained from Cambridge Isotope Laboratories, degassed and stored over 4 Å molecular sieves, except for CD$_2$Cl$_2$, which was stored over 3 Å molecular sieves. Benzyl potassium (KBN) was prepared according to a reported literature procedure. All commercial reagents were used as received and were obtained from Sigma Aldrich or Acros, with exception of 2-aminonicotinaldehyde, which was obtained from Key Organics. D$_2$ was obtained from Sigma Aldrich (Isotec™, 99.96 atom % D) and H$_2$ from Linde (Research grade 99.999%). NMR data was recorded on an Agilent MRF 400 equipped with a OneNMR probe and Optima Tune system or a Varian VNMR-S-400 equipped with a PFG probe. All resonances in $^1$H-NMR were referenced to residual solvent peaks (7.26 for CDCl$_3$, 7.16 for C$_6$D$_6$, 5.32 for CD$_2$Cl$_2$ and 3.58 for THF-$d_8$). IR-data was recorded on a PerkinElmer SpectrumTwo Infrared Spectrophotometer equipped with an ATR-probe. Elemental analysis was performed by MEDAC ltd. in the United Kingdom.

**2-methyl-1,8-naphthyridine**

All manipulations were performed under aerobic conditions using technical grade solvents. The synthesis was performed according to a modified literature procedure.

\[
\begin{align*}
\text{CO} & \quad + \quad \text{N} & \quad \text{NH}_2 \\
& \quad \text{L-Proline} \\
\text{N} & \quad \text{N} & \quad \text{N}
\end{align*}
\]

A 500 mL round-bottom flask was charged with 2-aminonicotinaldehyde (6.64 g, 54.3 mmol), EtOH (200 mL), L-proline (6.23 g, 54.1 mmol) and acetone (120 mL). The mixture was heated at reflux for 16 hours under vigorous stirring. After cooling to ambient temperature, the mixture was concentrated under reduced pressure to give an orange solid, which was dissolved in water (100 mL). The aqueous solution was extracted with CH$_2$Cl$_2$ (3x50 mL) and the combined organic layers were washed with brine (50 mL). The organic fraction was dried over Na$_2$SO$_4$ and concentrated under reduced pressure to yield an off-yellow solid. The solid was dissolved in a boiling mixture of EtOAc (40 mL) and PE 40-60 (60 mL). Slow cooling to ambient temperature resulted in the formation of a white crystalline solid. The mother liquor was
decanted off, the residue was washed with PE 40-60 (10 mL) and dried in vacuum to give a white solid (4.53 g). The washings were combined with the mother liquor, which was subsequently stored at 5 °C. After 24 h a second crop of crystalline material was collected by decanting off the mother liquor. The solid was washed with PE 40-60 (10 mL) and dried in vacuum to give a white solid (1.40 g). Combined yield: 5.93 g, 76%.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): δ 9.07 (dd, $^3$J$_{H,H}$ = 4.3 Hz, $^4$J$_{H,H}$ = 2.0 Hz, 1H), 8.13 (dd, $^3$J$_{H,H}$ = 8.1 Hz, $^4$J$_{H,H}$ = 2.0 Hz, 1H), 8.06 (d, $^3$J$_{H,H}$ = 8.3 Hz, 1H), 7.42 (dd, $^3$J$_{H,H}$ = 8.1, 4.3 Hz, 1H), 7.37 (d, $^3$J$_{H,H}$ = 8.3 Hz, 1H), 2.81 (s, 3H). NMR data are consistent with literature.$^3$

Figure S1. The $^1$H NMR spectrum of 2-methyl-1,8-naphthyridine in CDCl$_3$ at 25 °C.

Synthesis of 2,7-dimethyl-1,8-naphthyridine

The synthesis was performed according to a modified literature procedure.$^3$

![Synthesis reaction](image)

A 250 mL Schlenk flask was charged with 2-methyl-1,8-naphthyridine (5.93 g, 41.1 mmol) and Et$_2$O (100 mL) under a N$_2$ atmosphere. The suspension was cooled to -78 °C after which a MeLi solution (1.6 M in Et$_2$O, 25.8 mL, 41.3 mmol) was added dropwise over the course of 20
minutes. The mixture was stirred for two hours at -78 °C after which the orange mixture was allowed to warm to ambient temperature. After 1.5 h water (2 mL) was added and the mixture was stirred vigorously for 0.5 h after which all volatiles were evaporated in vacuum yielding an orange solid. [From here onwards all manipulations were performed under aerobic conditions using technical grade solvents.] The solid was dissolved in acetone and a saturated solution of KMnO₄ in acetone was added dropwise until a purple colour persisted. The formed MnO₂ was filtered off and saturated aqueous bisulphite solution was added until the filtrate lost its purple colour. The mixture was filtered and concentrated in vacuum to give a yellow solid. The solid was washed with 300 mL Et₂O and extracted with 350 mL CH₂Cl₂. The CH₂Cl₂ extracts were combined, washed with a 1:1 (v/v%) water/brine mixture (3x100 mL), and dried over Na₂SO₄. All volatiles were removed in vacuum yielding an off-white solid (5.82 g, 90%).

**¹H NMR (400 MHz, CDCl₃, 298 K):** δ 8.02 (d, ³J_H,H = 8.2 Hz, 2H), 7.32 (d, ³J_H,H = 8.2 Hz, 2H), 2.79 (s, 6H). NMR data are consistent with literature.³

![Figure S2: The ¹H NMR spectrum of 2,7-dimethyl-1,8-naphthyridine in CDCl₃ at 25 °C.](image-url)
Synthesis of t-BuPNNP

Although 2,7-dimethyl-1,8-naphthyridine can be deprotonated on each methyl group by a reaction with 2 equiv of n-BuLi, the subsequent addition of 2 equiv P(t-Bu)_2Cl followed by aqueous work-up mainly yields a PNN monophospine ligand. ³¹P NMR analysis of the reaction mixture prior to aqueous work-up showed significant amounts of unreacted P(t-Bu)_2Cl. No further conversion was observed even when the mixture was heated at reflux for >48 h. Our hypothesis is that upon reaction with the first equiv of P(t-Bu)_2Cl a subsequent rapid deprotonation occurs of the more acidic P-CH₂-C group, preventing addition of the second phosphine. Hence, our synthesis involves in situ preparation of the PNN monophosphine, which is subsequently deprotonated twice (P-CH₂-C and C-CH₃) and reacted with one additional equiv P(t-Bu)_2Cl. A subsequent aqueous work-up predominantly gives the desired t-BuPNNP ligand. The isolated yield is low due the necessary washing steps that are needed for purification. Efforts to improve the isolated yield are ongoing.

A Schlenk flask was charged with 2,7-dimethyl-1,8-naphthyridine (0.5 g, 3.2 mmol) and THF (10 mL). The mixture was cooled to -78 °C and a solution of n-BuLi (1.6 M in hexanes, 2.2 mL, 3.5 mmol) was added dropwise over the course of 10 minutes. After the addition the red solution was allowed to warm to ambient temperature. The resulting dark red solution was cannulated dropwise over the course of 10 minutes into a stirred solution of P(t-Bu)_2Cl (0.66 mL, 3.47 mmol) in THF (5 mL) at -78 °C. After the addition was completed the mixture was allowed to warm to room temperature. After stirring for 1 h, the reaction mixture was cooled to -78 °C and a solution of n-BuLi (1.6 M in hexanes, 4.1 mL, 6.6 mmol) was added dropwise over the course of 12 minutes. The mixture was allowed to warm to ambient temperature, and was cannulated dropwise over the course of 20 minutes into a solution of P(t-Bu)_2Cl (0.66 mL, 3.47 mmol) in THF (5 mL) at -78 °C. The mixture was allowed to warm to ambient temperature and was quenched after 18 h by carefully adding degassed water (10 mL). After vigorous stirring for 1 h, the orange mixture was extracted with Et₂O (3x10 mL). The extracts were combined, dried over Na₂SO₄ and concentrated in vacuum to yield an orange solid, which was transferred into a N₂-filled glovebox. The solid was extracted by vigorous stirring with n-hexane
(10 mL, 20 min), Et₂O (10 mL, 20 min) and THF (10 mL, 10 min). The residual solid was dried in vacuum to give an off-white solid (0.22 g, 16%).

**1H NMR (400 MHz, CD₂Cl₂, 298 K):** δ 8.01 (d, JHH = 8.3 Hz, 2H), 7.59 (d, JHH = 8.3 Hz, 2H), 3.26 (d, JHP = 3.4 Hz, 4H), 1.16 (d, JHP = 11.0 Hz, 36H).

**13C{1H} NMR (101 MHz, CD₂Cl₂, 298 K):** δ 166.7 (d, J = 14.6 Hz), 155.8, 136.7, 123.1 (d, JCP = 9.2 Hz), 119.3, 33.8 (d, JCP = 26.3 Hz), 32.5 (d, JCP = 22.5 Hz), 30.0 (d, JCP = 13.6 Hz).

**31P{1H} NMR (162 MHz, CD₂Cl₂, 298 K):** δ 35.8 (s).

**Anal. Calcd. For C₂₆H₄₄N₂P₂:** C, 69.93; H, 9.93; N, 6.27. Found C, 69.46; H, 9.65; N, 6.26.

**IR-ATR (cm⁻¹):** 2980 (m), 2952 (m), 2893 (m), 2860 (m), 1604 (m), 1540 (w), 1505 (m), 1473 (w), 1386 (w), 1366 (m), 1313 (w), 1242 (w), 1175 (w), 865 (w), 811 (w).

Figure S3: The ¹H NMR spectrum of t-BuPNNP in CD₂Cl₂ at 25 °C.
Figure S4: The $^{31}$P NMR spectrum of $^{14}$BuPNNP in CD$_2$Cl$_2$ at 25 °C.

Figure S5: The $^{13}$C (APT) NMR spectrum of $^{14}$BuPNNP in CD$_2$Cl$_2$ at 25 °C.
Figure S6: The IR-spectrum of $t$-BuPNNP.

**Synthesis of complex 1**

A suspension of $t$-BuPNNP (43.9 mg, 98.3 µmol) in THF (2 mL) was added dropwise to a vigorously stirred suspension of CuCl (20.8 mg, 210 µmol) in THF (2 mL) at ambient temperature. After stirring for 16 h a pink solid was filtered off, which was washed with hexane (1 mL) and extracted with CH$_2$Cl$_2$ (3 mL). The CH$_2$Cl$_2$ extracts were filtered and concentrated in vacuum to give a pink solid (49 mg, 78%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): δ 8.28 (d, $^3$J$_{H,H} = 8.3$ Hz, 2H), 7.57 (d, $^3$J$_{H,H} = 8.3$ Hz, 2H), 3.48 (d, $^2$J$_{H,P} = 7.7$ Hz, 4H), 1.32 (d, $^3$J$_{H,P} = 13.6$ Hz, 36H).

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$, 298 K): δ 165.3, 152.7, 139.3, 124.5, 122.2, 33.7 (d, $^1$J$_{C,P} = 8.2$ Hz), 33.2 (d, $^1$J$_{C,P} = 11.8$ Hz), 29.6 (d, $^2$J$_{C,P} = 8.1$ Hz).

$^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 298 K): δ 26.1 (bs).

Anal. Calcd. For C$_{26}$H$_{44}$Cl$_2$Cu$_2$N$_2$P$_2$: C, 48.45; H, 6.88; N, 4.35. Found C, 48.12; H, 6.63; N, 4.33.

IR-ATR (cm$^{-1}$): 2938 (m), 2897 (w), 2862 (w), 1727 (w), 1598 (w), 1541 (w), 1504 (w), 1467 (w), 1432 (w), 1368 (w), 1296 (w), 1130 (w), 863 (w), 820 (w).
Figure S7: The $^1$H NMR spectrum of complex 1 in CD$_2$Cl$_2$ at 25 °C.

Figure S8: The $^{31}$P NMR spectrum of complex 1 in CD$_2$Cl$_2$ at 25 °C.
Figure S9: The $^{13}$C NMR spectrum of complex 1 in CD$_2$Cl$_2$ at 25 °C, signals indicated with a star belong to hexane.

Figure S10: The IR-spectrum of complex 1.
Synthesis of complex 2

A suspension of KOtBu (14.0 mg, 125 µmol) in benzene (1 mL) was added dropwise to a vigorously stirred suspension of 1 (40.1 mg, 62.2 µmol) in benzene (1 mL). After 1 h the dark red mixture was filtered and concentrated in vacuum yielding 2 as a red film (36.2 mg, 90%).

$^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 6.75 (d, $^3$J$_{H,H}$ = 7.1 Hz, 1H), 6.53 (d, $^3$J$_{H,H}$ = 9.1 Hz, 1H), 6.43 (d, $^3$J$_{H,H}$ = 9.1 Hz, 1H), 5.94 (d, $^3$J$_{H,H}$ = 7.1 Hz, 1H), 4.29 (d, $^2$J$_{H,P}$ = 1.8 Hz, 1H), 2.57 (d, $^2$J$_{H,P}$ = 7.4 Hz, 2H), 1.88 (s, 9H), 1.33 (d, $^3$J$_{H,P}$ = 13.1 Hz, 18H), 0.91 (d, $^3$J$_{H,P}$ = 13.1 Hz, 18H).

$^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, 298 K): δ 166.7 (d, $^1$J$_{C,P}$ = 2.3 Hz), 134.0, 129.2 (d, $^3$J$_{C,P}$ = 2.4 Hz), 127.5 (d, $^1$J$_{C,P}$ = 9.5 Hz), 119.3, 110.4 (d, $^3$J$_{C,P}$ = 3.7 Hz), 81.4 (d, $^1$J$_{C,P}$ = 41.4 Hz), 72.1, 36.9, 33.5 (d, $^1$J$_{C,P}$ = 14.9 Hz), 32.4 (d, $^1$J$_{C,P}$ = 9.6 Hz), 32.4 (d, $^1$J$_{C,P}$ = 16.0 Hz), 30.3 (d, $^2$J$_{C,P}$ = 8.9 Hz), 29.6 (d, $^2$J$_{C,P}$ = 7.8 Hz).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, 298 K): δ 26.9 (bs), 7.7 (bs).

Anal. Calcd. For C$_{30}$H$_{52}$Cu$_2$N$_2$OP$_2$: C, 55.80; H, 8.12; N, 4.34. Found C, 56.07; H, 8.68; N, 4.20

IR-ATR (cm$^{-1}$): 2932 (m), 2859 (m), 1615 (m), 1583 (w), 1529 (m), 1490 (m), 1468 (m), 1444 (m), 1411 (s), 1389 (m), 1360 (m), 1318 (m), 1272 (w), 1181 (w), 1134 (m), 1017 (w), 934 (w), 861 (w), 828 (m), 792 (w), 766 (w), 660 (w), 516 (w), 493 (w), 473 (w), 436(w).
Figure S11: The $^1$H NMR spectrum of complex 2 in C$_6$D$_6$ at 25 °C.

Figure S12: The $^{31}$P NMR of complex 2 in C$_6$D$_6$ at 25 °C.
Figure S13: The $^{13}$C (APT) NMR spectrum of complex 2 in $\text{C}_6\text{D}_6$ at 25 °C.

Figure S14: The IR-spectrum of complex 2.
Synthesis of complex 3 • THF*

A solution of benzyl potassium (2.9 mg, 22 µmol) in THF (1 mL) was added dropwise to a solution of 2 (15.4 mg, 23.8 µmol) in THF (1 mL) at -40 °C. The resulting orange solution was left to warm up to room temperature and was subsequently concentrated \textit{in vacuo} to yield 3 as an orange film (17.3 mg, 95%). \textbf{NOTE:} Due to the highly reactive nature of 3 it is best prepared \textit{in situ}. Samples stored inside and N₂-filled glovebox at -40 °C show gradual decomposition to 2 over the course of several weeks.

\textbf{1H NMR (400 MHz, THF-\textit{d}$_8$, 298 K):} \(\delta 6.12 \text{ (d, } 3J_{H,H} = 8.4 \text{ Hz, } 2\text{H}), 5.56 \text{ (d, } 3J_{H,H} = 8.4 \text{ Hz, } 2\text{H}), 3.27 \text{ (d, } 2J_{H,P} = 1.3 \text{ Hz, } 2\text{H}), 1.53 \text{ (s, } 9\text{H}), 1.20 \text{ (d, } 3J_{H,P} = 12.6 \text{ Hz, } 36\text{H}). \) * the amount of THF is based on integration of the THF resonances in the 1H NMR spectrum.

\textbf{13C\{}^{1H}\text{ NMR (101 MHz, THF-\textit{d}$_8$, 298 K):} \(\delta 170.2 \text{ (d, } J = 14.9 \text{ Hz), } 131.4 \text{ (d, } 4J_{C,P} = 3.4 \text{ Hz), } 110.9 \text{ (d, } 2J_{C,P} = 9.4 \text{ Hz), } 103.9, 72.0, 64.4 \text{ (d, } 1J_{C,P} = 49.0 \text{ Hz), } 36.6, 34.1 \text{ (d, } 1J_{C,P} = 15.5 \text{ Hz), } 30.6 \text{ (d, } 2J_{C,P} = 8.7 \text{ Hz), } 26.6. \)

\textbf{31P\{}^{1H}\text{ NMR (162 MHz, THF-\textit{d}$_8$, 298 K):} \(\delta 14.4 \text{ (bs).} \)

The reactive nature of 3 precluded obtaining a satisfactory elemental analysis.
Figure S15: The $^1$H NMR spectrum of 3 • THF in THF-d$_8$ at 25 °C, resonances indicated with a triangle belong to THF-H$_8$, resonances indicated with a star belong to THF-d$_7$.

Figure S16: The $^{31}$P NMR spectrum of 3 • THF in THF-d$_8$ at 25 °C.
Figure S17: The $^{13}$C (APT) NMR spectrum of 3 • THF in THF-d$_8$ at 25 °C.
Synthesis of complex 4

H₂SiPh₂ (7.1 µL, 38 µmol) was added to a solution of 2 (24.1 mg, 35.2 µmol) in THF (2 mL) at ambient temperature. After stirring the red mixture for 1 h, volatiles were removed in vacuum. The residue was washed with cold pentane (3x1 mL) and dried in vacuum yielding 4 as a red solid (14.5 mg, 67%).

¹H NMR (400 MHz, C₆D₆, 298 K): δ 6.75 (d, ³J_H,H = 7.1 Hz, 1H), 6.45 (d, ³J_H,H = 9.1 Hz, 1H), 6.37 (d, ³J_H,H = 9.1 Hz, 1H), 6.12 (d, ³J_H,H = 7.1 Hz, 1H), 4.27 (s, 1H), 3.45 (d, ²J_H,H = 15.3 Hz, 1H), 2.87 (dd, ²J_H,H = 15.3, ²J_H,P 8.0 Hz, 1H), 1.48 (d, ³J_H,P = 11.7 Hz, 9H), 1.31 (d, ³J_H,P = 12.5 Hz, 9H), 1.08 (d, ³J_H,P = 11.7 Hz, 9H), 1.06 (d, ³J_H,P = 13.0 Hz, 9H).

¹H NMR (400 MHz, THF-d₈, 298 K): δ 6.88 (d, ³J_H,H = 7.1 Hz, 1H), 6.44 (dd, ³J_H,H = 9.1, ⁴J_H,H = 1.8 Hz, 1H), 6.29 – 6.23 (m, 2H), 3.96 (d, ²J_H,P = 2.6 Hz, 1H), 3.39 (d, ²J_H,H = 15.4 Hz, 1H), 3.11 (dd, ²J_H,H = 15.4, ²J_H,P = 8.2 Hz, 1H), 1.49 (d, ³J_H,P = 11.7 Hz, 9H), 1.12 (d, ³J_H,P = 11.5 Hz, 9H), 1.11 (d, ³J_H,P = 12.4 Hz, 9H), 0.77 (d, ³J_H,P = 13.0 Hz, 9H).

¹³C{¹H} NMR (101 MHz, THF-d₈, 298 K): δ 165.8 (d, J = 17.1 Hz), 158.4 (m), 158.1 (d, ²J_C,P = 3.5 Hz), 133.8, 129.3, 126.4 (d, J = 9.3 Hz), 119.2, 110.5, 82.1 (d, ¹J_C,P = 35.7 Hz), 34.5 (d, ¹J_C,P = 8.0 Hz), 34.3 (d, ¹J_C,P = 9.1 Hz), 33.3 (d, ¹J_C,P = 7.3 Hz), 32.8 (d, ¹J_C,P = 10.4 Hz), 32.7, 31.4 (d, ²J_C,P = 7.7 Hz), 30.7 (d, ²J_C,P = 8.8 Hz), 30.2 (d, ²J_C,P = 9.5 Hz), 29.8 (d, ²J_C,P = 9.6 Hz).

³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ 38.7 (bs), 12.3 (bs).

The reactive nature of 4 precluded obtaining a satisfactory elemental analysis.

IR-ATR (cm⁻¹): 2940 (m), 2892 (m), 2861 (m), 1618 (m), 1584 (w), 1537 (m), 1500 (s), 1469 (m), 1420 (s), 1361 (w), 1321 (m), 1179 (w), 1130 (m), 825 (w), 789 (w)
Figure S18: The $^1$H-NMR spectrum of complex 4 in C$_6$D$_6$ at 25 °C.

Figure S19: The $^1$H-NMR spectrum of complex 4 in THF-d$_8$ at 25 °C, resonances marked with a star are assigned to pentane.
Figure S20: The $^{31}$P-NMR spectrum of complex 4 in C$_6$D$_6$ at 25 °C.

Figure S21: The $^{13}$C (APT) NMR spectrum of complex 4 in THF-d$_8$ at 25 °C, resonances with a rectangle are assigned to traces of HSiPh$_2$Or-Bu.
Figure S22: The IR-spectrum of complex 4

Reaction of 2 with D₂SiPh₂:

Complex $d$-4 was prepared in situ by adding D₂SiPh₂ (5.2 µL, 28 µmol) to a solution of 2 (18.0 mg, 28 µmol) in benzene (0.6 mL) and was subsequently analysed by $^2$H-NMR spectroscopy.

Figure S23: The $^2$H-NMR spectrum of in situ prepared $d$-4 in C₆H₆ at 25 °C. The resonance indicated with a triangle is assigned to the deuteride of $d$-4 and the resonance marked with a star is assigned to the natural abundance of deuterium in benzene.
Protonation of 2 with NEt₃HCl:
A suspension of NEt₃HCl (3.4 mg, 25 µmol) in benzene (1 mL) was added dropwise to a solution of 2 (7.9 mg, 12 µmol) in benzene (1 mL). After stirring for 2 hours the mixture had turned into a dark pink suspension and the volatiles were removed in vacuo. The resulting pink solid was extracted with DCM and filtrated over a pipette filter. Subsequently, the filtrate was concentrated in vacuo yielding 1 as a pink solid (7.2 mg, 92%).

Protonation of 3 with NEt₃HCl:
Solid NEt₃HCl (4.3 mg, 31 µmol) was added to a solution of freshly prepared 3 • THF (21.2 mg, 28.0 µmol) and 1,4-dimethoxybenzene (4.3 mg, 31 µmol; internal standard) in THF-d₈ (0.6 mL), resulting in an immediate color change to dark red. Analysis of the reaction mixture by ¹H NMR spectroscopy showed quantitative conversion towards 2.
Reaction of 3 with H₂:

A J. Young NMR tube was charged with a solution of freshly prepared 3 • THF (10.9 mg, 14.4 µmol) and 1,4-dimethoxybenzene (1.9 mg, 14 µmol; internal standard) in THF-d₈ (0.7 mL). The mixture was subjected to three freeze-pump-thaw cycles and was backfilled with H₂ (1 bar). The sample was then heated at 40 °C for 30 h showing full conversion of 3 • THF and yielding 4 in 79 % spectroscopic yield.

Figure S24: The ¹H-NMR spectra measured before (top) and after (middle) heating a THF-d₈ solution of 3 • THF under a H₂ atmosphere at 40 °C for 30 h (recorded at 25°C). The bottom spectrum is of independently synthesized 4 through the H₂SiPh₂ route. Resonances marked with a star are assigned to 3 • THF, resonances marked with a rectangle are assigned to 4 and resonances marked with a triangle are assigned to decomposition products of 3 due to trace moisture introduced during H₂ addition.
Reaction of 3 with D₂

A J. Young NMR tube was charged with a solution of freshly prepared 3 • THF (19.8 mg, 26.2 µmol) in THF-d₈ (0.6 mL). The mixture was subjected to three freeze-pump-thaw cycles and was backfilled with D₂ (1 bar). The sample was then heated at 40 °C for 48 h showing full conversion of 3 • THF to 4.

Figure S25: The ¹H-NMR spectrum measured after heating a THF-d₈ solution of 3 • THF under an D₂ atmosphere at 40 °C for 48 h (recorded at 25°C). The spectrum shows clean conversion to complex 4 but with lower integration of the resonances of the ligand arms (at δ = 3.95, 3.40 and 3.11 ppm) due to partial deuterium incorporation.
Figure S26: The $^2$H-NMR spectrum measured after heating a THF-d$_8$ solution of 3 • THF under an D$_2$ atmosphere at 40 °C for 72 h (recorded in THF-H$_8$ at 25°C). Resonances indicated with a star are assigned to residual THF-d$_8$ and the natural abundance of deuterium in THF. The resonance indicated with a triangle is assigned to the deuteride of 4.
**Figure S27**: The $^2$H-NMR spectrum of a sample of 4 (recorded in C$_6$H$_6$ at 25°C) that was prepared by heating a THF-D$_8$ solution of 3 • THF under an D$_2$ atmosphere at 40 °C for 48 h. The resonance indicated with a star is assigned to the natural abundance of deuterium in benzene. The resonance indicated with a circle is assigned to the deuteride of 4 and the resonances indicated with a triangle are attributed to partial deuterium incorporation in the ligand arms of 4.

**Figure S28**: Schematic representation of the metric parameters within the expanded pincer ligands in complexes 1-3 for facile comparison of the how the intraligand bond lengths change upon partial (2) and full (3) dearomatization. NOTE: the bond lengths in the naphthyridine core in complex 1 are rather localized, which is a typical feature for bicyclic aromatics that is, for example, also observed in naphthalene (see: Cruickshank, D. W. J.; Sparks, R. A. ("Experimental and Theoretical Determinations of Bond Lengths in Naphthalene, Anthracene and Other Hydrocarbons"). Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences. 258 (1293): 270–285).
Crystallographic details

X-ray crystal structure determination of complex 1 (l1009b)

C_{26}H_{44}Cl_2Cu_2N_2P_2, Fw = 644.55, brown needle, 0.53 × 0.10 × 0.07 mm^3, tetragonal, P 4 2_1m (no. 113), a = b = 13.00573(12), c = 8.78874(11) Å, V = 1486.61(3) Å^3, Z = 2, D_x = 1.440 g/cm^3, µ = 1.74 mm^{-1}. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and 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 Eval15 software^4 was used for the intensity integration. A numerical absorption correction and scaling was performed with SADABS^5 (correction range 0.67-0.93). A total of 25797 reflections were measured, 1824 reflections were unique (R_{int} = 0.036), of which 1799 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT. Least-squares refinement was performed with SHELXL-2018^7 against F^2 of all reflections. The structure in the crystal appeared to be affected by whole-molecule disorder. The minor disorder component related to the major component approximately by a twofold rotation about uvw = [1,1,0]. Non-hydrogen atoms in the major disorder component were refined freely with anisotropic displacement parameters. The atoms of the minor disorder component were refined isotropically. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 137 Parameters were refined with 237 restraints (affecting the displacement parameters and the geometry of the disorder). R1/wR2 [I > 2σ(I)]: 0.0422 / 0.1098. R1/wR2 [all refl.]: 0.0427 / 0.1101. S = 1.158. Ratio between disorder components 0.674(5):0.326(5). Flack parameter^8 from a refinement as inversion twin, x = 0.47(5). Residual electron density between -0.56 and 0.33 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.^9

X-ray crystal structure determination of complex 2 (l1020a)

C_{30}H_{52}Cu_2N_2OP_2, Fw = 645.75, red plate, 0.70 × 0.34 × 0.10 mm^3, triclinic, P T̅̅̅̅ (no. 2), a = 13.6987(3), b = 15.6363(4), c = 16.2459(3) Å, α = 74.472(1), β = 80.623(1), γ = 80.239(1) °, V = 3278.86(12) Å^3, Z = 4, D_x = 1.308 g/cm^3, µ = 1.42 mm^{-1}. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and 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 Eval15 software⁴ was used for the intensity integration. A numerical absorption correction and scaling was performed with SADABS⁵ (correction range 0.53-0.90). A total of 91575 reflections were measured, 15052 reflections were unique (Rint = 0.026), of which 13483 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.⁶ Least-squares refinement was performed with SHELXL-2018⁷ against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. A total of 91575 reflections were measured, 15052 reflections were unique (Rint = 0.026), of which 13483 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.⁶ Least-squares refinement was performed with SHELXL-2018⁷ against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 697 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0219 / 0.0571. R1/wR2 [all refl.]: 0.0261 / 0.0590. S = 1.026. Residual electron density between -0.25 and 0.39 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.⁹

**X-ray crystal structure determination of complex 3 (11028b)**

[C₂₀H₄₀KO₈][C₃₀H₅₁Cu₂N₂OP₂], Fw = 1092.36, orange needle, 0.51 × 0.07 × 0.06 mm³, monoclinic, P2₁/n (no. 14), a = 14.1042(6), b = 15.6155(6), c = 26.8207(9) Å, β = 103.294(2) °, V = 5748.8(4) Å³, Z = 4, Dₓ = 1.262 g/cm³, µ = 0.92 mm⁻¹. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin 0/λ)max = 0.65 Å⁻¹. The Eval15 software⁴ was used for the intensity integration. A numerical absorption correction and scaling was performed with SADABS⁵ (correction range 0.74-1.00). A total of 67553 reflections were measured, 13227 reflections were unique (Rint = 0.097), of which 7455 were observed [I>2σ(I)]. The reflection data are characterized by pseudo-translational symmetry according to h+l=2n. The structure was solved with Patterson superposition methods using SHELXT.⁶ Least-squares refinement was performed with SHELXL-2018⁷ against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. One THF ligand in the cation and the t-butanolate in the anion were refined with disorder models. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 690 Parameters were refined with 420 restraints (concerning displacement parameters and geometries in the disordered groups). R1/wR2 [I > 2σ(I)]: 0.0568 / 0.1302. R1/wR2 [all refl.]: 0.1238 / 0.1568. S = 1.027. Residual electron density between -0.69 and 0.67 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.⁹
X-ray crystal structure determination of complex 4 (I1037a)

C_{52}H_{88}Cu_{4}N_{4}P_{4}, Fw = 1147.30, orange plate, 0.24 × 0.10 × 0.03 mm³, monoclinic, P2₁/n (no. 14), a = 12.2067(3), b = 20.0818(5), c = 23.2547(5) Å, β = 102.456(1) °, V = 5566.3(2) Å³, Z = 4, D_x = 1.369 g/cm³, µ = 1.66 mm⁻¹. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and 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 Eval15 software⁴ was used for the intensity integration. A split-mosaic model was used for the prediction of reflection profiles. A numerical absorption correction and scaling was performed with SADABS⁵ (correction range 0.70-0.95). A total of 94856 reflections were measured, 12792 reflections were unique (R_{int} = 0.091), of which 8741 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.⁶ Least-squares refinement was performed with SHELXL-2018⁷ against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The metal-bonded hydrogen atoms were located in difference-Fourier maps and refined freely with isotropic displacement parameters. All other hydrogen atoms were introduced in calculated positions and refined with a riding model. 609 Parameters were refined with no restraints. R₁/wR₂ [I > 2σ(I)]: 0.0464 / 0.0925. R₁/wR₂ [all refl.]: 0.0844 / 0.1057. S = 1.020. Residual electron density between -0.40 and 0.71 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.⁹

CCDC 1919274-1919277 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Computational Details

DFT calculations were performed with the ORCA program package, version 4.0.1.2. Optimized geometries were computed using the BP86 functional and the scalar relativistically recontracted version of the Aldrichs triple-ζ basis set, def2-TZVP, were used on all atoms. Initial geometries were obtained from the X-ray crystallographic models. The SCF calculations were tightly converged (TightSCF) with unrestricted spin (UKS). Optimizations were tightly converged (TightOpt).

Comparison of the experimental and DFT-calculated metric parameters of complex 4

The DFT optimized geometry (BP86, def2-TZVP) of complex 4 matches well with the experimentally found metric parameters (Table S1 and Figure S29, left). When the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ) was employed, the optimized geometry matched less well (Figure S29, right), giving a near tetrahedron-shaped core with a Cu11-Cu12 distance of 2.716 Å, which is significantly shorter than the experimentally obtained distance of 3.4144(3) Å and the calculated distance without the D3BJ correction (3.3520 Å).

Table S1: Experimental and DFT (BP86, def2-TZVP) calculated distances between atoms

| Atom 1 | Atom 2 | XRD (Å) | DFT (Å) |
|--------|--------|---------|---------|
| H1     | Cu12   | 1.61(4) | 1.6490  |
| H1     | Cu22   | 1.76(4) | 1.7573  |
| H1     | Cu21   | 1.79(4) | 1.8092  |
| H2     | Cu11   | 1.66(4) | 1.6510  |
| H2     | Cu21   | 1.76(4) | 1.7561  |
| H2     | Cu22   | 1.81(4) | 1.8138  |
| Cu21   | Cu22   | 2.4778(6) | 2.4975 |
| Cu12   | Cu21   | 2.7338(6) | 2.7062 |
| Cu22   | Cu12   | 2.5121(7) | 2.5381 |
| Cu11   | Cu22   | 2.7310(6) | 2.7011 |
| Cu11   | Cu21   | 2.5106(5) | 2.542  |
| Cu11   | Cu12   | 3.4144(6) | 3.3520 |
| Cu22   | P22    | 2.271(1) | 2.3240 |
| Cu22   | N22    | 2.124(2) | 2.1038 |
| Cu12   | N12    | 2.046(2) | 2.0668 |
| Cu12   | P12    | 2.260(1) | 2.3229 |
| Cu11   | P11    | 2.2588(9) | 2.3000 |
| Cu11   | N11    | 2.051(3) | 2.0653 |
| Cu21   | N21    | 2.118(3) | 2.1047 |
| Cu21   | P21    | 2.2846(9) | 2.3003 |
Figure S29: Structural overlays of the X-ray crystallographic models (blue) with the DFT calculated models (BP86, def2-TZVP) without (left) and with (right) the D3BJ dispersion correction.
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