Supporting Information for:

Isomerism and Dynamic Behavior of Bridging Phosphaalkynes Bound to a Dicopper Complex

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1) Experimental details, synthetic procedures, and characterization

General Considerations. Unless otherwise stated, all reactions and manipulations were carried out in a dry nitrogen or argon atmosphere employing either standard Schlenk techniques or VAC Atmosphere or MBRAUN nitrogen or argon-filled gloveboxes.¹

Pentane (HPLC grade), toluene (ACS grade), and acetonitrile (HPLC grade) were purchased from Fischer Scientific. Diethyl ether (HPLC grade) and dichloromethane (HPLC grade) were purchased from Honeywell. Hexanes (HPLC grade) were purchased from JT Baker. Tetrahydrofuran (ChromAR[®]) (THF) was purchased from Macron Fine Chemicals, and *ortho*-difluorobenzene (*o*-C₆H₄F₂) was purchased from Oakwood. Pentane, toluene, diethyl ether, tetrahydrofuran, acetonitrile, dichloromethane, and *ortho*-difluorobenzene were dried and deaerated using a JC Meyers Phoenix SDS solvent purification system. Hexanes were dried and deaerated using a VAC Atmosphere solvent purification system. All other solvents were obtained from commercial suppliers, distilled or transferred under reduced pressure from appropriate drying reagents, and stored in PTFE-valved flasks.

Cupric oxide (analytical reagent grade, wire form) was purchased from Mallinckrodt Chemical Works. Triflimidic acid (95+%) was purchased from Matrix Scientific.

Standard literature procedures were followed to synthesize $[Cu_2(\mu - \eta^1: \eta^1-MeCN)DPFN][NTf_2]_2^2$, MeCP,³ tBuCP⁴ and AdCP.⁵ Unless otherwise noted, all other reagents were obtained from commercial suppliers and used without further purification.

Analytical Methods Details. Carbon, hydrogen, and nitrogen elemental analyses were performed by the College of Chemistry's Microanalytical Facility at the University of California, Berkeley or at the elemental analysis facility of the University of Regensburg on a Vario EL III apparatus.

NMR Spectroscopy. Unless otherwise stated, NMR spectra were acquired between 294 and 298.5 K using Bruker AV-400, AV-500, AV-600, AV-700 or AV-900 spectrometers. ¹H and ¹³C NMR spectra were referenced to residual solvent peaks. ⁶ ¹⁹F and ³¹P NMR spectra were referenced to the IUPAC-recommended unified scale (reference compounds: CCl₃F and H₃PO₄ external, respectively) employing the samples' tetramethylsilane-referenced ¹H NMR spectrum and the Absolute Reference tool in MestReNova (v. 12.0.4). All NMR spectra were analyzed with MestReNova (v. 12.0.4).

IR Spectroscopy. Infrared spectra of all compounds were recorded via ATR employing either an A225/Q Platinum ATR accessory with a Bruker Vertex 80 FTIR Spectrometer equipped with a room temperature DLaTGS detector using OPUS software (v. 7.2), or a ThermoFischer Scientific ATR diamond accessory with a Thermoscientific Nicolet iS5 equipped with a DTGS KBr detector using OMNIC software (v. 9.6).

X-Ray Crystallography. X-ray diffraction data for complex **2** were collected at the X-ray structure analysis department of the University of Regensburg, using a Rigaku Oxford Diffraction GV50 equipped with a TitanS2 CCD detector and a SuperNova Cu K β microfocus source ($\lambda = 1.39222$ Å). X-ray diffraction data for complexes **3**, **4**, and **5** were collected at the Advanced Light Source (ALS), using a Bruker D8 diffractometer coupled to a Bruker PhotonII CPAD detector with Si(111)-monochromated 17 keV synchrotron radiation at beamline 12.2.1. X-ray diffraction data for complex **6** were collected at the UC Berkeley CheXRay facility using a Bruker AXS diffractometer with a Kappa geometry goniostat coupled to an APEX-II CCD detector with micro-focus Mo K α ($\lambda = 0.71073$ Å) radiation monochromated by a system of QUAZAR multilayer mirrors. Crystals of **3**, **4**, **5**, and **6** were kept at 100(2) K throughout collection, and the crystal of **2** was

kept at 123(2) K throughout collection. Data collection strategy determination, integration, scaling, and space group determination for **3**, **4**, **5**, and **6** were performed with Bruker APEX3 software (v. 2016.1), and for **2** with CrysAlisPro (v. 171.41.21a). Structures were solved with SHELXT-2014 and refined with SHELXL-2018, with refinement of F^2 on all data by full-matrix least squares.⁷ The 3D molecular structure figures were visualized with ORTEP 3.2. All crystallography figures were annotated with Adobe Illustrator CC 2018.

Co-crystallizing disordered solvent molecules and disordered triflimide anions were observed in some solid-state structures and were modeled atomistically, unless otherwise noted. Specific details of each experiment can be found below (Table S1) and in the crystallographic information files.

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Compound	Detector Distance (mm)	Image Width (°)	Exposure Time (s)		
2	62	1	110		
3	40	1 or 4 depending on angle	1		
4	40	1 or 4 depending on angle	1		
5	40	1 or 4 depending on angle	1		
6	40	0.75	30		

Table S1: X-Ray Crystallography Experimental Details

Synthesis of $[Cu_2(\mu-\eta^2:\eta^2-MeCP)DPFN](NTf_2)_2$ (2)

A 0.13 M solution of MeCP in THF was prepared. An aliquot of this solution (2.0 mL, 0.26 mmol, 3.1 equiv) was added slowly to a stirred bright orange solution of $[Cu_2(\mu-\eta^1:\eta^1-MeCN)DPFN](NTf_2)_2$ (102 mg, 0.083 mmol) in THF (15 mL). By the end of the addition, the resulting solution became bright yellow. The mixture was stirred for an additional 1.5 h and then filtered, and the filtrate was concentrated *in vacuo*. The resulting yellow powder was triturated twice with 25 mL hexanes and residual volatile compounds were removed *in vacuo* to afford $[Cu_2(\mu-\eta^2:\eta^2-MeCP)DPFN][NTf_2]_2$ as a yellow powder in 71% yield (73.7 mg, 0.059 mmol). Crystals suitable for single crystal X-ray diffraction studies were obtained from vapor diffusion of diethyl ether into an $o-C_6H_4F_2$ solution of $[Cu_2(\mu-\eta^2:\eta^2-MeCP)DPFN](NTf_2)_2$ at 21 °C.

¹H NMR (400.13 MHz, 40 °C, THF-*d*₈) δ 9.16 (d, *J* = 5.0 Hz, 4H, 6-pyridyl-C–*H*), 9.08 (d, *J* = 8.7 Hz, 2H, 4-naphth-C–*H*), 8.64 (dd, *J* = 8.7, 3.3 Hz, 2H, 3-naphth-C–*H*), 8.25 (dd, *J* = 8.0, 3.1 Hz, 4H, 3-pyridyl-C–*H*), 8.19 (td, *J* = 7.9, 1.7 Hz, 4H, 4-pyridyl-C–*H*), 7.75 (ddd, *J* = 7.2, 5.2, 1.3 Hz, 4H, 5-pyridyl-C–*H*), 2.45 (d, *J* = 10.8 Hz, 3H, PCC*H*₃). ¹³C{¹H} NMR (100.63 MHz, 40 °C, THF-*d*₈) δ 161.22 (d, *J* = 30.2 Hz, 2-naphth-*C*), 155.50 (d, *J* = 77.4 Hz, PCCH₃), 153.35 (d, *J* = 29.5 Hz, 2-pyridyl-*C*), 151.70 (br, 6-pyridyl-*C*–H and 8a-naphth-*C*, overlapping), 144.93 (d, *J* = 3.7 Hz, 4-naphth-*C*–H), 141.94 (d, *J* = 3.2 Hz, 4-pyridyl-*C*–H), 126.90 (5-pyridyl-*C*–H), 124.85 (4a-naphth-*C*), 121.96 (d, *J* = 14.5 Hz, 3-pyridyl-*C*–H), 121.22 (d, *J* = 16.8 Hz, 3-naphth-*C*–H), 120.90 (q, *J* = 322.2 Hz, $-SO_2-CF_3$), 94.06 (d, *J* = 189.1 Hz, (pyridyl)₂(naphth)*C*–F), 22.27 (d, *J* = 12.9 Hz, PCCH₃). ¹⁹F NMR (376.62 MHz, 21 °C, THF-*d*₈) δ -80.21 (12F, $-SO_2-CF_3$), -173.20 (d, *J* = 3.3 Hz, (pyridyl)₂(naphth)*C*–*F*). ³¹P NMR (162.04 MHz, 40 °C, THF-*d*₈) δ -29.08 (q, *J* = 11.1 Hz, PCCH₃). Anal. Calcd for C₃₆H₂₃Cu₂F₁₄N₈O₈PS₄: C, 34.65; H, 1.86; N, 8.98. Found: C, 34.74; H, 1.94; N, 8.65.

Synthesis of $[Cu_2(\mu-\eta^2:\eta^2-tBuCP)DPFN](NTf_2)_2$ (3)

To a stirred bright orange solution of $[Cu_2(\mu-\eta^1:\eta^1-MeCN)DPFN](NTf_2)_2$ (47 mg, 0.038 mmol) in 15 mL THF, ^tBuCP (0.06 mL, 0.06 mmol, 1.5 equiv) was added. By the end of the addition, the resulting solution is yellow. The mixture was stirred for an additional 0.5 hour then filtered, and the filtrate concentrated *in* *vacuo*. The tan powder was triturated with 25 mL pentane, then with 25 mL diethyl ether, and then volatiles were removed *in vacuo* to afford $[Cu_2(\mu-\eta^2:\eta^{2-t}BuCP)DPFN](NTf_2)_2$ as a pale orange powder in 68% yield (37 mg, 0.026 mmol). Crystals suitable for single crystal X-ray diffraction studies were obtained from layering of diethyl ether over a THF solution of $[Cu_2(\mu-\eta^2:\eta^{2-t}BuCP)DPFN](NTf_2)_2$ at -35 °C.

¹H NMR (400.13 MHz, THF-*d*₈) δ 9.23 (dd, *J* = 5.2, 1.4 Hz, 4H, 6-pyridyl-*C*–*H*), 9.15 (d, *J* = 8.7 Hz, 2H, 4-naphth-*C*–*H*), 8.68 (dd, *J* = 8.7, 3.2 Hz, 2H, 3-naphth-*C*–*H*), 8.22 (dd, *J* = 7.8, 3.1 Hz, 4H, 3-pyridyl-*C*–*H*), 8.17 (td, *J* = 7.8, 1.6 Hz, 4H, 4-pyridyl-*C*–*H*), 7.75 (ddd, *J* = 7.0, 5.2, 1.5 Hz, 4H, 5-pyridyl-*C*–*H*), 1.14 (s, 9H, PCC(*C*H₃)₃). ¹³C{¹H} NMR (100.63 MHz, THF-*d*₈) δ 177.24 (PCC(*C*H₃)₃)^a, 161.07 (d, *J* = 31.5 Hz, 2-naphth-*C*), 153.38 (d, *J* = 28.9 Hz, 2-pyridyl-*C*), 152. 28 (8a-naphth-*C*), 151.87 (6-pyridyl-*C*–H), 145.14 (4-naphth-*C*–H), 141.92 (d, *J* = 3.4 Hz, 4-pyridyl-*C*–H), 126.66, (5-pyridyl-*C*–H), 124.67 (4a-naphth-*C*), 121.96 (d, *J* = 13.9 Hz, 3-pyridyl-*C*–H), 121.84 (d, *J* = 16.6 Hz, 3-naphth-*C*–H), 120.89 (q, *J* = 322.3 Hz, –SO₂–*C*F₃), 94.07 (d, *J* = 189.3 Hz, (pyridyl)₂(naphth)*C*–F), 43.54 (d, *J* = 11.3 Hz, PCC(CH₃)₃), 35.20 (PCC(*C*H₃)₃). ¹⁹F NMR (376.62 MHz, THF-*d*₈) δ -80.17 (12F, –SO₂–*C*F₃), -172.36 (d, *J* = 3.5 Hz, 2F, (pyridyl)₂(naphth)*C*–*F*). ³¹P NMR (162.04 MHz, THF-*d*₈) δ -11.02 (*P*CC(CH₃)₃).

Anal. Calcd for C₃₉H₂₉Cu₂F₁₄N₈O₈PS₄: C, 36.31; H, 2.27; N, 8.69. Found: C, 36.62; H, 2.40; N, 8.54.

Synthesis of $[Cu_2(\mu-\eta^2:\eta^2-AdCP)DPFN](NTf_2)_2$ (4)

A solution of AdCP (8.0 mg, 0.046 mmol, 1.1 equiv) in 3 mL THF was added slowly to a stirred bright orange solution of $[Cu_2(\mu-\eta^{1}:\eta^{1}-MeCN)DPFN](NTf_2)_2$ (50.2 mg, 0.041 mmol) in 5 mL THF. By the end of the addition, the solution is yellow. The mixture was stirred for an additional 1 hour then filtered, and the filtrate concentrated *in vacuo*. The resulting light-orange powder was triturated twice with 10 mL diethyl ether and then volatiles were removed *in vacuo* to afford $[Cu_2(\mu-\eta^{2}:\eta^{2}-AdCP)DPFN](NTf_2)_2$ as a pale orange powder in 91% yield (50.6 mg, 0.0369 mmol). Crystals suitable for single crystal X-ray diffraction studies were obtained from vapor diffusion of hexanes into a fluorobenzene solution of $[Cu_2(\mu-\eta^{2}:\eta^{2}-AdCP)DPFN](NTf_2)_2$ at 21 °C.

¹H NMR (600.13 MHz, THF-*d*₈) δ 9.22 (d, *J* = 5.2 Hz, 4H, 6-pyridyl-C–*H*), 9.12 (d, *J* = 8.7 Hz, 2H, 4-naphth-C– *H*), 8.66 (dd, *J* = 8.6, 3.2 Hz, 2H, 3-naphth-C–*H*), 8.24 (dd, *J* = 8.1, 3.1 Hz, 4H, 3-pyridyl-C–*H*), 8.19 (td, *J* = 7.9, 1.6 Hz, 4H, 4-pyridyl-C–*H*), 7.79 (ddd, *J* = 7.1, 5.2, 1.3 Hz, 4H, 5-pyridyl-C–*H*), 2.01 (s, 6H, 2-Ad–C*H*₂), 1.81 (s, 3H, 3-Ad–C*H*), 1.55 (dd, *J* = 19.4, 11.4 Hz, 6H, 4-Ad–C*H*₂). ¹³C{¹H} NMR (150.92 MHz, THF-*d*₈) δ 178.03 (d, *J* = 79.7 Hz, PCAd), 161.15 (d, *J* = 31.2 Hz, 2-naphth-C), 153.32 (d, *J* = 29.2 Hz, 2-pyridyl-C), 152.14 (8a-naphth-*C*), 151.55 (6-pyridyl-C–H), 144.93 (d, *J* = 3.4 Hz, 4-naphth-*C*–H), 142.01 (d, *J* = 3.5 Hz, 4-pyridyl-C–H), 126.78 (5-pyridyl-C–H), 124.59 (4a-naphth-C), 122.14 (d, *J* = 15.9 Hz, 3-pyridyl-C–H), 121.63 (d, *J* = 15.9 Hz, 3-naphth-*C*–H), 120.96 (q, *J* = 322.2 Hz, $-SO_2-CF_3$), 94.02 (d, *J* = 189.4 Hz, (pyridyl)₂(naphth)*C*–F), 47.88 (2-Ad–CH₂), 46.61 (d, *J* = 9.4 Hz, 1-Ad–C), 36.19 (4-Ad–CH₂), 29.75 (3-Ad–CH). ¹⁹F NMR (564.61 MHz, THF-*d*₈) δ -80.17 (12F, $-SO_2-CF_3$), -172.00 (2F, (pyridyl)₂(naphth)C–F). ³¹P NMR (242.94 MHz, THF-*d*₈) δ -8.90 (br, *P*CAd).

Anal. Calcd for C₄₅H₃₅Cu₂F₁₄N₈O₈PS₄: C, 39.51; H, 2.58; N, 8.19. Found: C, 39.27; H, 2.55; N, 7.92.

Synthesis of $[Cu_2(\mu-\eta^1:\eta^1-AdCN)DPFN](NTf_2)_2(5)$

A solution of AdCN (5.2 mg, 0.032 mmol, 1.3 equiv) in 2 mL THF was added slowly to a stirred bright orange solution of $[Cu_2(\mu-\eta^{1}:\eta^{1}-MeCN)DPFN](NTf_2)_2$ (30.1 mg, 0.025 mmol) in 4 mL THF. By the end of the addition, the solution is lighter orange. The mixture was stirred for an additional 1 hour then filtered, and the filtrate concentrated *in vacuo*. The resulting light-orange powder was triturated with twice with 10 mL diethyl ether and then volatiles were removed *in vacuo* to afford $[Cu_2(\mu-\eta^{1}:\eta^{1}-AdCN)DPFN][NTf_2]_2$ as an orange powder in 85% yield (28.0 mg, 0.021 mmol). Crystals suitable for single crystal X-ray diffraction

^a Resonance observed by ¹³C{¹H} HMBC.

studies were obtained from vapor diffusion of hexanes into an $o-C_6H_4F_2$ solution of $[Cu_2(\mu-\eta^1:\eta^1-AdCN)DPFN](NTf_2)_2$ at 21 °C.

¹H NMR (600.13 MHz, THF-*d*₈) δ 9.18 (d, *J* = 4.9 Hz, 4H, 6-pyridyl-C–*H*), 8.91 (d, *J* = 8.6 Hz, 2H, 4-naphth-C– *H*), 8.48 (dd, *J* = 8.6, 3.0 Hz, 2H, 3-naphth-C–*H*), 8.23 (dd, *J* = 8.2, 3.3 Hz, 4H, 3-pyridyl-C–*H*), 8.15 (td, *J* = 7.9, 1.7 Hz, 4H, 4-pyridyl-C–*H*), 7.78 (dd, *J* = 7.3, 5.3 Hz, 4H, 5-pyridyl-C–*H*), 2.56 (s, 6H, 2-Ad–CH₂), 2.14 (s, 3H, 3-Ad–C*H*), 1.95 (d, *J* = 11.6 Hz, 3H, 4-Ad–C*H*₂), 1.80 (d, *J* = 12.8 Hz, 3H, 4-Ad–C*H*₂). ¹³C{¹H} NMR (150.92 MHz, THF-*d*₈) δ 159.99 (d, *J* = 31.1 Hz, 2-naphth-*C*), 153.00 (d, *J* = 29.4 Hz, 2-pyridyl-*C*), 151.10 (d, *J* = 3.2 Hz, 6-pyridyl-*C*–H), 149.52 (8a-naphth-*C*), 142.80 (d, *J* = 3.3 Hz, 4-naphth-*C*–H), 140.72 (d, *J* = 3.3 Hz, 4-pyridyl-*C*–H), 126.69 (5-pyridyl-*C*–H), 124.14 (4a-naphth-*C*), 121.40 (d, *J* = 14.4 Hz, 3-pyridyl-*C*–H), 120.97 (q, *J* = 322.0 Hz; $-SO_2-CF_3$), 120.53 (d, *J* = 14.5 Hz, 3-naphth-*C*–H), 93.27 (d, *J* = 188.2 Hz, (pyridyl)₂(naphth)*C*–F), 39.33 (2-Ad–*C*H₂), 35.84 (4-Ad–*C*H₂), 34.44 (1-Ad–*C*), 27.83 (3-Ad–*C*H). ¹⁹F NMR (564.61 MHz, THF-*d*₈) δ -80.10 (12F, $-SO_2-CF_3$), -175.55 (2F, d, *J* = 3.6 Hz, (pyridyl)₂(naphth)*C*–*F*). Anal. Calcd for C₄₅H₃₅Cu₂F₁₄N₉O₈S₄: C, 40.00; H, 2.61; N, 9.33. Found: C, 39.74; H, 2.54; N, 9.46.

Synthesis of $[Cu_2(\mu-\eta^2:\eta^2-(MeC\equiv CMe))DPFN](NTf_2)_2$ (6)

To a bright orange, stirred solution of $[Cu_2(\mu-\eta^1:\eta^1-MeCN)DPFN](NTf_2)_2$ (25.1 mg, 0.0203 mmol) in $o-C_6H_4F_2$ (2 mL) 2-butyne (16.0 g, 0.296 mmol, 15 equiv) were added. Upon addition of 2-butyne, the reaction mixture became yellow. The solution was stirred for 1.5 hours and then concentrated *in vacuo*. The resulting yellow oil was triturated twice with diethyl ether (1.5 mL). Residual volatile compounds were removed *in vacuo* affording **6** as a yellow powder in 96 % yield (24.3 mg, 0.0195 mmol). Crystals suitable for single crystal X-ray diffraction studies were obtained from vapor diffusion of pentane into a THF solution of **6** at -35 °C.

¹H NMR (900.25 MHz, THF-*d*₈) δ 9.07 (d, J = 5.1 Hz, 4H, 6-pyridyl-C–*H*), 9.05 (d, J = 8.6 Hz, 2H, 4-naphth-C–*H*), 8.60 (dd, J = 8.6, 3.2 Hz, 2H, 3-naphth-C–*H*), 8.25 (dd, J = 8.3, 3.4 Hz, 4H, 3-pyridyl-C–*H*), 8.18 (td, J = 7.9, 1.7 Hz, 4H, 4-pyridyl-C–*H*), 7.75 (ddd, J = 7.7, 5.2, 1.2 Hz, 4H, 5-pyridyl-C–*H*), 2.87 (s, 6H, CH₃CCCH₃). ¹³C{¹H} NMR (226.39 MHz, THF-*d*₈) δ 160.91 (d, *J* = 30.3 Hz, 2-naphth-*C*), 153.60 (d, *J* = 29.4 Hz, 2-pyridyl-*C*), 151.20 (8a-naphth-*C* and 6-pyridyl-C–H, overlapping), 144.08 (4-naphth-*C*–H), 141.46 (4-pyridyl-*C*–H), 126.60 (5-pyridyl-*C*–H), 124.40 (4a-naphth-*C*), 121.85 (d, *J* = 15.1 Hz, 3-pyridyl-*C*–H), 120.97 (d, *J* = 15.9 Hz, 3-naphth-*C*–H), 120.85 (q, *J* = 322.1, 321.6 Hz, $-SO_2-CF_3$)), 93.66 (d, *J* = 188.9 Hz, (pyridyl)₂(naphth)*C*–F), 79.49 (CH₃*CC*CH₃), 11.87 (*C*H₃CCCH₃). ¹⁹F NMR (376.45 MHz, THF-*d*₈) δ -80.21 (12F, $-SO_2-CF_3$), -173.16 (d, *J* = 3.7 Hz, 2F, (pyridyl)₂(naphth)*C*–F).

Anal. Calcd for C₃₈H₂₆Cu₂F₁₄N₈O₈S₄: C, 36.69; H, 2.11; N, 9.01. Found: C, 36.48; H, 2.28; N, 9.04.

2) Supplementary figures





















Figure S6. Excerpts of the ambient temperature and low temperature (-80 °C) ¹H NMR spectra of $[Cu_2(\mu - \eta^2: \eta^2: 2-butyne)]$ (NTf₂]₂ **6** in *d*₈-THF



Figure S7. Excerpts of the low temperature NOESY NMR spectra of (a) 2, (b) 3 and (c) 4 in d₈-THF





Details: Spectra acquired at $-60 \degree C$ (**2**) or $-90 \degree C$ (**3**, **4**). Significant correlation between the alkyl group of R–C=P and one set of 6- and 5-pyridyl positions is observed for **2** and **4**, while correlations to both sets of 6- and 5- pyridyl positions are observed for **3**, as denoted by the relative integrations observed for the NOESY peaks.



Figure S8. Low temperature (-60 °C) DOSY NMR spectrum of $[Cu_2(\mu-\eta^2:\eta^2-AdCP)DPFN][NTf_2]_2$ **4** in d_{8^-}

Details: Top: full spectrum. Bottom: excerpt of the aromatic region showing nearly identical diffusion coefficients, hence hydrodynamic radii, for the two species.

Figure S9. Full NMR spectra (top) and excerpt (bottom) of the high temperature (35 °C) and low temperature (-60 °C) ¹³C NMR spectra of $[Cu_2(\mu-\eta^2:\eta^2-AdCP)DPFN][NTf_2]_2$ **4** in d_8 -THF.



3) Computational details

General considerations. DFT calculations were performed at the Molecular Graphics and Computation Facility of the University of California, Berkeley using the Gaussian 16 suite of *ab initio* programs.⁸ Atoms were modeled using the parameter free density functional model PBE0⁹ along with Grimme's dispersion with Becke-Johnson damping (D3(BJ)),¹⁰ unless otherwise noted, and a combination of all-electron def2-SVP, def2-TZVP, def2-TZVPD and def2-QZVPPD basis sets¹¹ depending on atomic number and distance to the dicopper core, as noted in the details of each figure. The DFT structures were optimized either as gas phase structures or with a Self Consistent Reaction Field (SCRF) default solvation model set to THF.¹² NMR computations were performed using the Gauge-Independent Atomic Orbital (GIAO) method and the spinspin option;¹³ only the coupling constant of interest was computed using the readatoms option. Natural Bond Order (NBO) and Natural Localized Molecular Orbital (NLMO) analysis were performed using nbo6.¹⁴ The calculated metal complexes have a full-size DPFN ligand and bridging fragment without simplification, and were optimized as dications, omitting non-coordinating triflimide anions. The 3D molecular structure figures displayed were drawn using Mercury v. 4.1.3, omitting all hydrogens atoms. Molecular orbital surfaces were visualized in Gaussview with an isovalue of 0.05, and when necessary, relative shading of orbitals to display symmetry-allowed interactions were adjusted manually using Photofiltre 7 v. 7.2.1. Overlay root-mean square deviation (RMDS) and maximum deviations (Max. D) were computed using Mercury v. 4.1.3.

A) Computational details for geometry optimizations and NMR computations of complexes 2 – 6, as well as NBO computations for complex 6.

Metric	2-trans	2-end	2-cis
Electronic Energy (Hartrees)	-5380.303063	-5380.279683	-5380.310165
Gibbs Free Energy (Hartrees)	-5379.873151	-5379.854565	-5379.876925
Number of imaginary frequencies	0	1	0
Relative Electronic Energy (kcal/mol)	+4.6	+19.1	0
Relative Gibbs Free Energy (kcal/mol)	+2.4	+14.0	0
Cu…Cu (Å)	2.969	2.542	2.688
Cu–C _{averaged} (Å)	2.062	3.557	2.013
Cu–P _{averaged} (Å)	2.260	2.189	2.312
P≡C (Å)	1.626	1.540	1.627
P≡C–C (°)	149.2	179.8	156.0
Naphth bend (°)	0.8	0.8	18.1

 Table S2. Computed energies, selected bond distances and selected angles for proposed structural isomers 2-trans, 2-end and 2-cis

Details: Geometries optimized with a THF scrf solvation model. Basis sets: def2-TZVP (Cu, P, N) and def2-SVP (C, H, F).

Figure S10. Computed geometries of three conformations of **2** (front view and side-view): **2-***trans* (μ - η^2 : η^2 , Me and naphthyridine on opposite sides of the Cu₂N₄ plane); **2-***end* (μ - η^1 : η^1 ; **2-***cis* (μ - η^2 : η^2 , Me and naphthyridine on the same side of the Cu₂N₄ plane)



Details: Geometries optimized with a THF scrf solvation model. Basis sets: def2-TZVP (Cu, P, N) and def2-SVP (C, H, F).

Metric	3-trans	3-cis
Electronic Energy (Hartrees)	-5498.021348	-5498.024599
Gibbs Free Energy (Hartrees)	-5497.510450	-5497.512475
Number of imaginary frequencies	0	0
Relative Electronic Energy (kcal/mol)	+2.0	0
Relative Gibbs Free Energy (kcal/mol)	+1.3	0
Cu…Cu (Å)	2.6708	2.6158
Cu–C _{averaged} (Å)	2.1261	2.0552
Cu–P _{averaged} (Å)	2.2702	2.3076
P≡C (Å)	1.6189	1.6302
P≡C−C (°)	146.1	150.0
Naphth bend (°)	18.7	30.6

 Table S3. Computed energies, selected bond distances and selected angles for proposed structural isomers 3-trans and 3-cis

Details: Geometries optimized with a THF scrf solvation model. Basis sets: def2-TZVP (Cu, P, N) and def2-SVP (C, H, F).

Figure S11. Computed geometries of two conformations of **3** (front and side views): **3**-*trans* (μ - η^2 : η^2 , ^tBu and naphthyridine on opposite sides of the Cu₂N₄ plane) and **3**-*cis*(μ - η^2 : η^2 , ^tBu and naphthyridine on the same side of the Cu₂N₄ plane)



Details: Geometries optimized with a THF scrf solvation model. Basis sets: def2-TZVP (Cu, P, N) and def2-SVP (C, H, F).

Table S4. Computed energies, selected computed bond distances and angles for proposed structural isomers **4-***trans*, **4-***end* and **4-***cis*. Top: metrics using a combination of def2-TZVP and def2-SVP basis sets for best comparison of the relative energies of **4-***trans*, **4-***end* and **4-***cis* with relative energies of isomers of **2** and **3**. Bottom: metrics using a combination of def2-QZVPPD, def2-TZVPD and def2-SVP basis sets for most accurate NMR computation results

Metric	4-trans	4-end	4-cis
Electronic Energy (Hartrees)	-5729.899701	-5729.880763	-5729.903783
Gibbs Free Energy (Hartrees)	-5729.281579	-5729.264266	-5729.283891
Number of imaginary frequencies	0	0	0
Relative Electronic Energy (kcal/mol)	+2.6	+14.4	0
Relative Gibbs Free Energy (kcal/mol)	+1.5	+12.3	0

Details: Geometries optimized with a THF scrf solvation model. Basis sets: def2-TZVP (Cu, P, N) and def2-SVP (C, H, F).

Metric	4-trans	4-end	4-cis
Electronic Energy (Hartrees)	-5730.207732	-5730.189946	-5730.213019
Gibbs Free Energy (Hartrees)	-5729.588935	-5729.574124	-5729.593842
Number of imaginary frequencies	0	0	0
Relative Electronic Energy (kcal/mol)	+3.3	+14.5	0
Relative Gibbs Free Energy (kcal/mol)	+3.1	+12.4	0
Cu…Cu (Å)	2.655	2.538	2.623
Cu–C _{averaged} (Å)	2.118	3.495	2.049
Cu–P _{averaged} (Å)	2.266	2.185	2.298
P≡C (Å)	1.615	1.542	1.628
P≡C–C (°)	146.5	175.2	150.2
Naphth bend (°)	19.2	1.9	28.8

Details: Geometries optimized with a THF scrf solvation model. Basis sets: def2-QZVPPD (Cu, P, C directly bound to P), def2-TZVPD (N, 4 C atoms closest to C=P bond) and def2-SVP (F, H, remaining C).





Details: Geometry optimized with a THF scrf solvation model. Basis sets: def2-QZVPPD (Cu, C involved in C=C), def2-TZVPD (N, terminal C atoms of butyne fragment) and def2-SVP (F, H, remaining C).

Geometry	Solvation	Enthalpy (Hartrees)	δ _c (ppm)	J _{C-P} (Hz)	J _{C-P,reduced} (Hz)
A +++++++	None	-5730.055852	190.4	92.6	73.6
4-trans	THF	-5730.207732	187.5	93.7	74.5
4-end	THF	-5730.189946	215.6	191.9	155.8
A = i=	None	-5730.058923	193.7	109.0	86.6
4-cis	THF	-5730.213019	189.1	106.7	84.8

Table S5. Selected final energies and computed NMR parameters in the gas phase and with a THF solvation model for proposed structural isomers **4**-*trans*, **4**-*end* and **4**-*cis*.

Details: Computed chemical shifts are referenced against the computed chemical shift of SiMe₄ with a B3LYP functional, a 6-311+G(2d,p) basis set, and the GIAO method.

Complex	RMSD (Å)	Max. D (Å)
2	0.1087	0.2822
3	0.1812 (w/ ^t Bu) 0.1486 (w/o ^t Bu)	0.5476 (w/ ^ք Bu) 0.2656 (w/o ^ք Bu)
4	0.1213 (w/ Ad) 0.1126 (w/o Ad)	0.3735 (w/ Ad) 0.3049 (w/o Ad)
6	0.1640	0.4809

Table S6. Overlay parameters of computed geometries of complexes 2 – 6 and their solid-state structures

Details: Geometries optimized with a THF scrf solvation model and basis sets as described in Table S2, Table S3, Table S4-bottom and Figure S12. For **3** and **4**, two sets of metrics are provided: one where the rotating R group (^tBu or Ad) on the RCP fragment is considered for the overlay, the other one where it is not.

Table S7. Overlay parameters of computed geometries **4**-*trans* and **4**-*cis* either in the gas phase (no solvation) or with a THC scrf solvation model

Geometry	RMSD (Å)	Max. D (Å)
4-trans	0.0451 (w/ Ad)	0.1155 (w/ Ad)
	0.0153 (w/o Ad)	0.0238 (w/o Ad)
. .	0.0334 (w/ Ad)	0.0786 (w/ Ad)
4 <i>-CIS</i>	0.0095 (w/o Ad)	0.0139 (w/o Ad)

Details: Geometries optimized either in the gas phase (no solvation) or with a THF scrf solvation model. Basis sets: def2-QZVPPD (Cu, P, C directly bound to P), def2-TZVPD (N, 4 C atoms closest to C=P bond) and def2-SVP (F, H, remaining C). Two sets of metrics are provided: one where the rotating Ad group on the AdCP fragment is considered for the overlay, the other one where it is not.

Table S8. Selected sections of the NBO-NLMO calculation output file for 6.

SECON	ID ORDER PERTU	RBATION TH	IEORY ANAL	YSIS OF FOCK MA	TRIX IN NBO BASIS	_/
Donor	orbital	Acceptor c	orbital	E(2) (kcal/mol)	E(NL)-E(L) (a.u.)	F(L,NL) (a.u)
2 to 3						
168. B	D (2) C 55- C 56	174. LV (1	1)Cu 69	3.68	0.74	0.047
169. B	D (3) C 55- C 56	174. LV (1	1)Cu 69	22.17	0.80	0.119
2 to 4						
168. B	D (2) C 55- C 56	175. LV (1	1)Cu 70	3.64	0.74	0.046
169. B	D (3) C 55- C 56	175. LV (1	1)Cu 70	22.30	0.80	0.119
3 to 2		·				
77. LP	(5)Cu 69	261.BD*(2) C 55- C 56	5 8.64	0.34	0.048
77. LP	(5)Cu 69	262. BD*(3) C 55- C 56	5 12.01	0.45	0.066
4 to 2						
82. LP	(5)Cu 70	261.BD*(2) C 55- C 56	5 8.59	0.34	0.048
82. LP	(5)Cu 70	262. BD*(3) C 55- C 56	5 12.09	0.45	0.066
Orbita	l label	Oc	cupancy	Energy level		
1.00				0.275.00		
168.	BD (2) C 55- C	56 1.9	94/33	-0.37586		
169.	BD(3)C55-C		33644	-0.43189		
201.			19095	0.01965		
202.		. 50 0.3	21222	0.13044		
//. 174	LP(5)CU69	1.0	52UZ8	-0.31701		
1/4.		0.2	24712	0.30413		
0Z. 17E	LP(3)CU70	1.0		-0.51/14		
175.	LV (1)CU 70	0.2	24772	0.30404		
Sorted	MOs:					
Sort	Occupancy	Energy	Origin	al number and la	bel	
147.	1.94733	-0.37586	168.	BD (2) C 55- C 56	5	
154.	1.83644	-0.43189	169.	BD (3) C 55- C 56	5	
155.	1.82028	-0.31701	77.	LP (5)Cu 69		
156.	1.81911	-0.31714	82.	LP (5)Cu 70		
182.	0.31225	0.13644	262.	BD*(3) C 55- C 5	6	
190.	0.24772	0.36464	175.	LV (1)Cu 70		
191.	0.24712	0.36413	174.	LV (1)Cu 69		
194.	0.19095	0.01965	261.	BD*(2) C 55- C 5	6	

Hybridization/Polarization Analysis of NLMOs in NAO Basis: NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions

77. (2.00000) 90.4209% LP (5)Cu 69 4.094% C 55 s(12.09%)p 7.22(87.30%)d 0.04(0.54%) f 0.01(0.07%)g 0.00(0.01%) 3.860% C 56 s(11.39%)p 7.74(88.21%)d 0.03(0.34%)

f 0.00(0.06%)g 0.00(0.00%) 90.422% Cu 69 s(0.19%)p 0.09(0.02%)d99.99(99.79%) f 0.01(0.00%)g 0.00(0.00%) 0.473% Cu 70 s(0.63%)p 1.84(1.15%)d99.99(97.97%) f 0.40(0.25%)g 0.00(0.00%) 82. (2.00000) 89.9486% LP (5)Cu 70 4.502% C 55 s(13.44%)p 6.40(86.01%)d 0.04(0.48%) f 0.00(0.06%)g 0.00(0.01%) 4.208% C 56 s(12.93%)p 6.71(86.70%)d 0.02(0.31%) f 0.00(0.05%)g 0.00(0.00%) 89.950% Cu 70 s(0.18%)p 0.10(0.02%)d99.99(99.79%) f 0.01(0.00%)g 0.00(0.00%) 168. (2.00000) 97.3580% BD (2) C 55- C 56 48.968% C 55 s(0.00%)p 1.00(99.35%)d 0.00(0.49%) f 0.00(0.16%)g 0.00(0.00%) 48.390% C 56 s(0.00%)p 1.00(99.38%)d 0.00(0.44%) f 0.00(0.18%)g 0.00(0.00%) 0.593% Cu 69 s(78.15%)p 0.16(12.84%)d 0.09(6.87%) f 0.03(2.14%)g 0.00(0.00%) 0.594% Cu 70 s(77.74%)p 0.17(13.06%)d 0.09(7.07%) f 0.03(2.13%)g 0.00(0.00%) 169. (2.00000) 91.0774% BD (3) C 55- C 56 44.422% C 55 s(12.06%)p 7.27(87.68%)d 0.01(0.16%) f 0.01(0.09%)g 0.00(0.01%) 46.660% C 56 s(13.07%)p 6.64(86.73%)d 0.01(0.10%) f 0.01(0.10%)g 0.00(0.01%) 3.820% Cu 69 s(97.08%)p 0.01(0.86%)d 0.02(1.80%) f 0.00(0.26%)g 0.00(0.00%) 3.843% Cu 70 s(97.12%)p 0.01(0.85%)d 0.02(1.77%) f 0.00(0.26%)g 0.00(0.00%)

Details: The triply bonded carbons in the butyne fragment are numbered C55 and C56; the butyne fragment is fragment 2 while fragments 3 and 4 each correspond to of one Cu center. Nomenclature of the orbitals are as follows: BD C55- C56: filled π orbital of the butyne fragment; BD* C55- C56: empty π * orbital of the butyne fragment; LP Cu: filled 3d orbital of a Cu center; LV Cu: empty 4s orbital of a Cu center. For the excerpts of NLMO analysis, only the contributions strictly greater to 0.4% are shown here.

Pyridine group	H _{methyl}	H _{pyridine}	Distance (Å)	
	H53	H31	2.3178	
	H53	H50	3.8761	
N4 and N6 pyridine	H55	H31	3.8758	
rings	H55	H50	2.3179	
	H54	H31	3.7374	
	H54	H50	3.7371	
Avg. Me – 6-py distances	3.31035			
	H53	H22	6.0882	
	H54	H22	6.0721	
N3 and N5 pyridine	H55	H22	6.5220	
rings	H55	H41	6.0883	
	H54	H41	6.0721	
	H53	H22	6.0882	
Avg. Me – 6-py distances to the N3 and N5 pyridine (away from Me) 6.15515				

Table S9. Distances between the methyl protons of the MeCP bridging group and the 6-pyridyl position of each set of pyridines for structure **2**-*cis* (DFT-optimization of the solid-state geometry adopted by **2**).

Details: H–H distances were measured on DFT-optimized structures using the single-crystal X-ray diffraction structure of **2** as input file to circumvent the systematic error encountered on H atom position and C–H bond lengths in X-ray diffraction data. As shown Table S6, there is an excellent overlay between the solid-state structure of **2** and its DFT-optimized version.

Pyridine group	H _{tert-butyl}	H _{pyridine}	Distance (Å)
	H75	H22	3.3901
	H58	H22	2.2652
	H57	H22	2.0870
	H55	H22	4.5591
	H54	H22	5.6023
	H73	H22	5.1805
	H74	H22	5.1069
	H61	H22	4.4422
N3 and N5 pyridine	H60	H22	5.5406
rings	H55	H41	5.3050
	H54	H41	5.4376
	H73	H41	5.2284
	H74	H41	3.7621
	H61	H41	2.4125
	H60	H41	4.0671
	H57	H41	1.9579
	H58	H41	3.6304
	H75	H41	3.5287
Avg. ^t Bu – 6-py distances	4.0835		
	H55	H31	2.7193
	H54	H31	3.4363
	H73	H31	4.4071
	H58	H31	4.2258
	H75	H31	5.4557
	H57	H31	5.4359
	H74	H31	5.9903
	H61	H31	5.9616
N4 and N6 pyridine	H60	H31	5.3074
rings	H58	H50	6.0913
	H75	H50	6.1186
	H57	H50	5.6591
	H55	H50	5.2302
	H54	H50	3.9221
	H73	H50	5.3147
	H74	H50	4.5219
	H61	H50	3.7410
	H60	H50	2.7687
Avg. ^t Bu – 6-py distances	to the N4 and N6 pyridine	e rings (closer to P)	4.7948

Table S10. Distances between the *tert*-butyl protons of the ^tBuCP bridging group and the 6-pyridyl position of each set of pyridines for structure **3**-*trans* (DFT-optimization of the solid-state geometry adopted by **3**).

Details: H–H distances were measured on DFT-optimized structures using the single-crystal X-ray diffraction structure of **3** as input file to circumvent the systematic error encountered on H atom position and C–H bond lengths in X-ray diffraction data. As shown Table S6, there is an excellent overlay between the solid-state structure of **3** and its DFT-optimized version.

Table S11. Distances between the 2-adamantyl protons of the AdCP bridging group and the 6-pyridyl position of each set of pyridines for complex **4-***trans* (DFT-optimization of the solid-state geometry adopted by **4**).

Pyridine group	Hadamantyl	Hpyridine	Distance (Å)
	H55	H31	2.6366
	H54	H31	3.3116
	H58	H31	4.1547
	H57	H31	5.3583
	H61	H31	5.8837
N4 and N6 pyridine	H60	H31	5.2058
rings	H54	H50	3.9436
	H55	H50	5.2582
	H60	H50	2.7297
	H61	H50	3.6934
	H58	H50	6.0573
	H57	H50	5.5897
Avg. Ad – 6-py distances	4.4852		
	H57	H22	2.0515
	H58	H22	2.2591
	H61	H22	4.4016
	H60	H22	5.5042
	H54	H22	5.5847
N3 and N5 pyridine	H55	H22	4.5612
rings	H60	H41	4.0679
	H61	H41	2.4141
	H57	H41	1.9560
	H58	H41	3.6398
	H55	H41	5.3250
	H54	H41	5.4508
Avg. Ad – 6-py distances	to the N3 and N5 pyridine	rings (away from P)	3.9347

Details: H–H distances were measured on DFT-optimized structures using the single-crystal X-ray diffraction structure of **4** as input file to circumvent the systematic error encountered on H atom position and C–H bond lengths in X-ray diffraction data. As shown Table S6, there is an excellent overlay between the solid-state structure of **4** and its DFT-optimized version.

B) Computational details for geometry optimization, NMR computations and training set determination for the benchmarking of computed NMR coupling constants.

Unless otherwise noted, all results reported in this subsection were based on calculations with PBE0-D3(BJ) and a mixed basis set of def2-QZVPPD on the principle C and P, i.e. those for which J_{CP} is being computed, def2-TZVPD for all atoms directly bonded to these two, and def2-SVP for all other atoms. Moreover, Gaussian's UltraFine DFT integration grid was used. This is the same level of theory used for the calculations reported above.

The 21-molecule training set used for linear regression is shown in Table S12. The geometry of all molecules was optimized, and the resulting structures were confirmed to be energy minima using vibrational analysis. The optimized structures are included in this SI as MDL MOL files in "structures.zip". After the optimization, each molecule's self-consistent-field solution was checked with stability analysis.¹⁵ All solutions were found to be stable to spin polarization; each training molecule is thus verified to be closed-shell singlet with doubly occupied DFT orbitals.

Structure	Source ¹⁶	Formal C-P bond	d _{CP} (Å)
		order	
allman_I	16c	single	1.9081
allman_II	16c	single	1.8865
allman_III	16c	single	1.8222
allman_VIII	16c	single	1.827
fuchs_5	16j	single	1.7871
appel_3	16a	triple	1.5421
pellerin_5b	16f	triple	1.5372
appel2_2	16b	triple	1.5414
allspach_8	16g	triple	1.5393
liang_1f	16m	triple	1.5385
regitz_3j	16i	triple	1.5356
regitz_3I	16i	triple	1.5386
regitz_3p	16i	triple	1.5391
regitz_3q	16i	triple	1.5464
regitz_3r	16i	triple	1.5442
paasch_3	16k	double	1.707
fuchs_3a	16j	double	1.6985
yoshifuji_3	16d	double	1.6284
oberg_5	16l	double	1.6964
knaap_6b	16e	double	1.6819
heinicke_2b	15h	double	1.7232

 Table S12. Molecules used in training set, with computed bond lengths.

Details: Structures are named according to first author and structure label from the pertinent reference.

Next, we computed the coupling constants for each training structure. The results are shown in Table S13.

Structure	J _{CP,exp}	F	S	Р	D	$J_{CP,calc}$
allman_I	-33.9	-53.8213	6.39224	-3.03426	0.377835	-50.0855
allman_II	-28.8	-41.0896	7.20122	-2.83947	0.380696	-36.3472
allman_III	-5.9	-21.5574	4.88464	-5.43664	0.385687	-21.7237
allman_VIII	-12.51	-26.7923	5.07051	-5.72959	0.373484	-27.0779
fuchs_5	-50	-62.2678	2.35787	-6.16279	0.44119	-65.6316
appel_3	13.9	-38.3969	64.1027	0.485068	0.0826613	26.2736
pellerin_5b	49	-28.6106	67.7967	21.3829	0.0652039	60.6341
appel2_2	48.3	-26.1006	66.6165	18.1594	0.107242	58.7825
allspach_8	39	-33.9939	64.6011	17.0327	0.13681	47.7768
liang_1f	38.1	-38.8359	66.6665	19.5714	0.139782	47.5417
regitz_3j	46.5	-28.2511	67.2886	19.4623	0.174159	58.674
regitz_3I	45.5	-29.731	66.3755	18.7502	0.108093	55.5028
regitz_3p	41.6	-33.2298	65.5488	17.9459	0.117011	50.382
regitz_3q	53.2	-22.4389	71.1044	19.2038	0.194621	68.0639
regitz_3r	46	-25.7626	63.9963	14.9351	0.138646	53.3073
paasch_3	-63	-52.6278	15.7319	-44.4945	0.285988	-81.1044
fuchs_3a	-102.5	-101.499	7.55703	-34.1766	0.329118	-127.789
yoshifuji_3	-58.1	-49.3208	26.1754	-44.8943	0.361713	-67.678
oberg_5	-36.1	-10.2648	42.25	-54.7735	0.350917	-22.4373
knaap_6b	-42.8	-16.7809	32.0113	-55.7446	0.348772	-40.1655
heinicke_2b	-50.2	-40.4357	9.22338	-41.0588	0.275521	-71.9956
4a	-76.8	-91.1995	19.8531	-21.9626	0.68355	-92.6254
4c	-83.3	-104.884	18.4578	-21.0051	0.6871	-106.7442

Table S13. Computed and experimental coupling constant data for the training set, and structures **4**-*trans* and **4**-*cis* of this work. The signs of the (originally unsigned) experimental data have been adjusted to match those of the computational data, as explained below.

Details: All values are in Hz. The terms in the middle columns are: Fermi Contact (*F*), Spin Dipolar (*S*), Paramagnetic spin-orbit (*P*), and Diamagnetic spin-orbit (*D*). $J_{CP,calc}$ is the sum of *F*, *S*, *P*, and *D*.

Verifying calculation quality

We also considered the effect solvation has on the computed coupling constants. For this, we performed additional calculations on the training-molecule subset consisting of the nine molecules with C-P triple bonds and only C atoms bound directly to the principle C and P (i.e. only excluding appel_3 from the triple-bond subset). For this, we used Gaussian's default implicit solvation model, the integral equation formalism variant of Polarizable Continuum Model (IEFPCM),¹⁷ and applied it both to the geometry optimizations and to the NMR calculations. The relationship between the resulting data and the corresponding experimental data is less linear than it is for the gas-phase data; for example, the R² value

for the solvated data is 0.7885, while it is 0.9257 for gas phase. Using SMD solvation¹⁸ on these 9 molecules, the R² value is 0.5253. In addition, the use of implicit solvation gives unphysical variation of the coupling constant. For example, for CH₃CP, $_{JCP,exp}$ = 49.0 Hz both in CD₂Cl₂and in CDCl₃,¹⁹ while the IEFPCM calculations give 54.0128 Hz and 55.2118 Hz for these two solvents, respectively. These observations support our use of the gas-phase calculated data for the empirical correction of the main text.

It is known that coupling constant calculations generally require more sophisticated basis sets to obtain reasonable accuracy.²⁰ For this purpose, Gaussian has the "nmr=mixed" option, which raises the basisset quality on atoms in a general way by de-contracting the orbitals and also in an NMR-specific way by adding core orbitals. For the same 9 triple-bond molecules above, we used this de-contracted and coresupplemented basis (from def2-QZVPPD) on the principle C and P to re-compute $J_{CP,calc}$. For these calculations, we also increased the DFT integration grid to Gaussian's SuperFine grid. Compared to the above data, the coupling constants are essentially shifted upwards by 2 Hz (range 1.9-2.2), and the associated linear fit has R² = 0.938, i.e. the data is essentially the same. This is not surprising given that the above data uses the already large def2-QZVPPD basis for the principle atoms. This validates our basisset and grid choices for the training set and various other structures discussed above and in the main text.

Multiple Linear Regression

In the main text, simple linear regression (SLR) is used to obtain an empirical correction for $J_{CP,calc}$. The NMR calculations produce more detailed information for the calculated coupling constants, namely the 4 standard contributions to *J*: Fermi Contact (*F*), Spin Dipolar (*S*), Paramagnetic spin-orbit (*P*), and Diamagnetic spin-orbit (*D*). This data is included in Table S13. With this, we can consider an empirical correction based on multiple linear regression (MLR) using these 4 variables. Here, we use the relationship $J_{CP,calc} = fF + sS + pP + dD$, and vary the coefficients *f*, *s*, *p*, *d* to minimize the error of the predicted values.

Looking at Table S13, the *F*,*S*,*P*,*D* data of molecules **4a** and **4c** bear a much stronger resemblance to those of the single and double bond molecules in the training set. This is particularly the case for the *P* values, which are positive for each triple-bond molecule and negative for all the single or double bond molecules, as is the case for **4a** and **4c**. We also note that the computed C-P bond lengths of 1.6152 Å and 1.6278 Å for **4a** and **4c**, respectively, are more in line with those of the double-bond training-set molecules. We therefore excluded all the triple-bond molecules from the training set for the MLR. The use of the full training set data may be better suited to more advanced, non-linear forms of multivariable regression.

For the MLR fit, one might be inclined to minimize the deviation between the unsigned experimental data and unsigned predicted data. This, however, would complicate the numerical regression procedure. Instead, we adjusted the experimental J_{CP} values to have the same sign as their computed counterparts and proceeded with standard MLR. If the predicted data has the same sign as the adjusted experimental data, which was the case here, this approach produces a mathematically equivalent result to minimizing the deviation of the unsigned numbers.

The optimized coefficients of the MLR are:

$$J_{CP,exp} = 0.93224 F - 0.25873 S + 0.52873 P + 40.37616 D$$
(Eq.)

This gives J_{CP} values of -74.169 Hz and -85.916 Hz for **4a** and **4c**, respectively. Observing the similarity in the SLR and MLR predictions for **4a** and **4c**, there evidently is significant cancellation of the above overall

irregularities when moving from the *F*,*S*,*P*,*D* data to the comparatively nondescript J_{CP} data used in the SLR. This similarity also reinforces our structure assignments from the NMR spectrum.

Influence of P–C distance on computed coupling constant

Figure S13. Graph view of P–C coupling constants as a function of P–C distance. No meaningful correlation of these two metrics is observed.



4) Single-crystal X-ray diffraction crystal structure figures and data tables

Figure SC1. Solid-state structure of $[Cu_2(\mu-\eta^2:\eta^2-MeCP)DPFN][NTf_2]_2$ (**2**) as determined by single crystal X-ray diffraction.





Details: Hydrogen atoms and two NTf₂⁻ counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1…Cu2: 2.6548(5), Cu1–P1: 2.2934(5), Cu2–P1: 2.2966(5), Cu1–C31: 2.003(2), Cu2–C31: 2.000(2), Cu1–N1: 2.101(1), Cu1–N3: 1.984(1), Cu1–N4: 2.127(1), Cu2–N2: 2.071(1), Cu2–N5: 1.989(1), Cu2–N6: 2.166(1), C31–P1: 1.631(2), C31–P1–C4: 42.53(2), P1–C31–C32: 154.5(1), Naphthyridine bent (angles between the planes defined by C1–C2–C20 and C7–C8–C9): 20.1

Table SC1. Crystal data and structure refinement for $[Cu_2(\mu-\eta^2:\eta^2-MeCP)DPFN][NTf_2]_2$ (2)

Empirical formula	$C_{36}H_{23}Cu_2F_{14}N_8O_8PS_4$		
Formula weight	1247.91		
Temperature	123(2) К		
Wavelength	1.39222 Å		
Crystal system	Monoclinic		
Space group	P21/c		
Unit cell dimensions	a = 19.7106(2) Å	α = 90°	
	b = 9.94890(10) Å	$\beta = 99.8080(10)^{\circ}$	
	c = 22.7748(2) Å	γ = 90°	
Volume	4400.83(7) Å ³		
Z	4		
Density (calculated)	1.883 Mg/m ³		
Absorption coefficient	3.233 mm ⁻¹		
F(000)	2488		
Crystal size	0.180 x 0.040 x 0.040 mm ³		
Theta range for data collection	3.557 to 74.203°.		
Index ranges	–27 ≤ h ≤ 27, –13 ≤ k ≤ 11, –30 ≤ l ≤ 28		
Reflections collected	29513		
Independent reflections	11820 [<i>R</i> (int) = 0.0239]		
Completeness to theta = 72.450°	98.4 %		
Absorption correction	Gaussian		
Max. and min. transmission	1.000 and 0.394		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	11820 / 0 / 659		
Goodness-of-fit on F ²	0.618		
Final R indices [I>2sigma(I)]	<i>R1</i> = 0.0327, <i>wR2</i> = 0.1036		
R indices (all data)	R1 = 0.0369, wR2 = 0.1130		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.563 and –0.541 e.Å ⁻³		

Figure SC2. Solid-state structure of $[Cu_2(\mu - \eta^2 : \eta^2 - tBuCP)DPFN][NTf_2]_2$ (**3**) as determined by single crystal X-ray diffraction.





Details: Hydrogen atoms, two disordered triflimide counterions and one co-crystallizing diethyl ether molecule have been omitted for clarity. One co-crystallizing disordered THF molecule per unit cell has been treated with SQUEEZE. Thermal ellipsoids are set at the 20% probability level. The C–P bridging fragment as well as the two Cu atoms are disordered and modelled in two parts; only the major component (76% occupancy) is displayed. Both components feature μ - η^2 : η^2 binding of the phosphaalkyne to the dicopper core in the *trans* geometry. This crystal structure likely contains total molecule disorder that cannot be modelled atomistically, explaining the discrepancy between *R1* and *Rint*.

Table SC2. Crystal data and structure refinement for $[Cu_2(\mu-\eta^2:\eta^2-tBuCP)DPFN][NTf_2]_2$ (3)

Empirical formula	C42 H20 C112 E14 No O9 P S4		
Eormula weight	$C_{43} = 139 C C 2 F_{14} = 108 C 3 F - 34$		
	1504.11		
lemperature	100(2) K		
Wavelength	0.7288 A		
Crystal system	Triclinic		
Space group	ΡĪ		
Unit cell dimensions	a = 12.4499(7) Å	α = 89.354(2)°	
	b = 12.6370(6) Å	β = 84.840(2)°	
	c = 18.5946(9) Å	γ = 72.243(2)°	
Volume	2774.4(2) Å ³		
Z	2		
Density (calculated)	1.633 Mg/m ³		
Absorption coefficient	1.122 mm ⁻¹		
F(000)	1376		
Crystal size	0.080 x 0.060 x 0.020 mm ³		
Theta range for data collection	1.768 to 26.162°.		
Index ranges	$-14 \le h \le 15, -15 \le k \le 15, 0 \le l \le 22$		
Reflections collected	10257		
Independent reflections	10257 [R(<i>int</i>) = 0.052]		
Completeness to theta = 26.100°	100.0 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.664887 and 0.591802		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	10257 / 157 / 845		
Goodness-of-fit on F ²	1.888		
Final R indices [I>2sigma(I)]	<i>R1</i> = 0.1273, <i>wR2</i> = 0.3950		
R indices (all data)	<i>R1</i> = 0.1446, <i>wR2</i> = 0.4173		
Extinction coefficient	n/a		
Largest diff. peak and hole	1.592 and –1.275 e.Å ⁻³		

Figure SC3. Solid-state structure of $[Cu_2(\mu - \eta^2: \eta^2 - AdCP)DPFN][NTf_2]_2$ (**4**) as determined by single crystal X-ray diffraction.





Details: Hydrogen atoms and two NTf₂⁻ counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Six molecules of disordered hexanes and fluorobenzene per unit cell have been treated with SQUEEZE in PLATON. Selected bond lengths [Å] and angles [°]: Cu1…Cu2: 2.6177(8), Cu1–P1: 2.270(1), Cu2–P1: 2.262(1), Cu1–C31: 2.106(4), Cu2–C31: 2.101(5), Cu1–N2: 2.099(4), Cu1–N3: 2.026(4), Cu1–N4: 2.127(4), Cu2–N1: 2.099(4), Cu2–N5: 2.010(4), Cu2–N6: 2.120(4), C31–P1: 1.628(4), P1–C31–C4: 55.3(1), P1–C31–C32: 143.1(3), Naphthyridine bent (angles between the planes defined by C1–C2–C20 and C7–C8–C9): 19.7

Table SC3. Crystal data and structure refinement for $[Cu_2(\mu-\eta^2:\eta^2-AdCP)DPFN][NTf_2]_2$ (4)

Empirical formula	$C_{45}H_{35}Cu_2F_{14}N_8O_8PS_4$		
Formula weight	1368.10		
Temperature	100(2) K		
Wavelength	0.7288 Å		
Crystal system	Monoclinic		
Space group	P21/n		
Unit cell dimensions	a = 18.6915(8) Å	α = 90°.	
	b = 16.5896(7) Å	β = 96.346(2)°.	
	c = 18.8035(9) Å	γ = 90°.	
Volume	5794.9(4) Å ³		
Z	4		
Density (calculated)	1.568 Mg/m ³		
Absorption coefficient	1.074 mm ⁻¹		
F(000)	2752		
Crystal size	0.100 x 0.080 x 0.040 mm ³		
Theta range for data collection	1.688 to 27.060°.		
Index ranges	–23 ≤ h ≤ 23, –20 ≤ k ≤ 20, –23 ≤ l ≤ 23		
Reflections collected	ollected 80765		
Independent reflections	11763 [<i>R</i> (int) = 0.0757]		
Completeness to theta = 27.060°	99.5 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.6746 and 0.5687		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	11763 / 91 / 794		
Goodness-of-fit on F ²	1.028		
Final R indices [I>2sigma(I)]	<i>R</i> 1 = 0.0748, <i>wR</i> 2 = 0.2019		
R indices (all data)	<i>R</i> 1 = 0.0853, <i>wR</i> 2 = 0.2109		
Extinction coefficient	n/a		
Largest diff. peak and hole	1.698 and –2.184 e.Å ⁻³		

Figure SC4. Solid-state structure of $[Cu_2(\mu - \eta^2: \eta^2 - AdCN)DPFN][NTf_2]_2$ (**5**) as determined by single crystal X-ray diffraction.





Details: Hydrogen atoms and two NTf_2^- counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1…Cu2: 2.4592(5), Cu1–N7: 1.941(2), Cu2–N7: 1.995(3), Cu1–C31: 2.976(3), Cu2–C31:2.925(3), Cu1–N1: 2.022(3), Cu1–N3: 2.072(3), Cu1–N4: 2.047(3), Cu2–N2: 2.019(3), Cu2–N5: 2.065(3), Cu2–N6: 2.060(3), C31–N1: 1.153(4), N7–C31–C32: 174.2(3), Naphthyridine bent (angles between the planes defined by C1–C2–C20 and C7–C8–C9): 2.4.

Table SC4. Crystal data and structure refinement for $[Cu_2(\mu-\eta^2:\eta^2-AdCN)DPFN][NTf_2]_2$ (5)

Empirical formula	$C_{45}H_{35}Cu_2F_{14}N_9O_8S_4$		
Formula weight	1351.14		
Temperature	100(2) K		
Wavelength	0.7288 Å		
Crystal system	Orthorhombic		
Space group	P2 ₁ 2 ₁ 2 ₁		
Unit cell dimensions	a = 10.9180(4) Å	α = 90°.	
	b = 20.4455(7) Å	β = 90°.	
	c = 23.1939(8) Å	γ = 90°.	
Volume	5177.4(3) Å ³		
Z	4		
Density (calculated)	1.733 Mg/m ³		
Absorption coefficient	1.170 mm ⁻¹		
F(000)	2720	2720	
Crystal size	0.100 x 0.080 x 0.040	0.100 x 0.080 x 0.040 mm ³	
Theta range for data collection	2.043 to 34.118°.		
Index ranges	–16 ≤ h ≤ 16, –31 ≤ k	≤ 31, −35 ≤ ≤ 35	
Reflections collected	97505		
Independent reflections	19659 [<i>R</i> (int) = 0.073	19659 [<i>R</i> (int) = 0.0738]	
Completeness to theta = 34.100°	99.6 %		
Absorption correction Semi-empirical fro		equivalents	
Max. and min. transmission	0.6673 and 0.5793		
Refinement method	Full-matrix least-squa	Full-matrix least-squares on F ²	
Data / restraints / parameters	19659 / 0 / 739	19659 / 0 / 739	
Goodness-of-fit on F ²	1.058	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.	1329	
R indices (all data)	R1 = 0.0538, wR2 = 0.	1374	
Absolute structure parameter	-0.002(5)		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.885 and –1.340 e.Å	-3	

Figure SC5. Solid-state structure of $[Cu_2(\mu - \eta^2 : \eta^2 - 2 - butyne)DPFN][NTf_2]_2$ (**6**) as determined by single crystal X-ray diffraction.



Details: Hydrogen atoms, one co-crystallizing THF molecule and two NTf₂⁻ counterions have been omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1…Cu2: 2.6687(4), Cu1–C32: 2.007(3), Cu2–C32: 2.036(3), Cu1–C33: 2.059(2), Cu2–C33: 2.054(3), Cu1–N1: 2.189(2), Cu1–N3: 2.091(2), Cu1–N4: 1.996(2), Cu2–N2: 2.097(2), Cu2–N5: 2.161(2), Cu2–N6: 2.016(3), C32–C33: 1.261(4), C32–C33–C4: 57.7(2), C31–C32–C33: 154.8(3), C32–C33–C34: 152.6(3) Naphthyridine bent (angles between the planes defined by C1–C2–C9 and C6–C7–C20): 15.8

Table SC5. Crystal data and structure refinement for $[Cu_2(\mu - \eta^2: \eta^2 - 2 - butyne)DPFN][NTf_2]_2$ (6)

Empirical formula	C ₄₂ H ₃₄ Cu ₂ F ₁₄ N ₈ O ₉ S	4	
Formula weight	1316.09		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	РĪ		
Unit cell dimensions	a = 12.5211(4) Å	α = 76.518(2)°.	
	b = 14.8116(5) Å	β = 67.701(2)°.	
	c = 15.6245(5) Å	γ = 76.651(2)°.	
Volume	2574.23(15) Å ³		
Z	2		
Density (calculated)	1.698 Mg/m ³		
Absorption coefficient	1.100 mm ⁻¹		
F(000)	1324		
Crystal size	0.110 x 0.080 x 0.030	0.110 x 0.080 x 0.030 mm ³	
Theta range for data collection	1.427 to 25.350°.	1.427 to 25.350°.	
Index ranges	–15 ≤ h ≤ 15, –17 ≤ k ≤ 17, –18 ≤ l ≤ 18		
Reflections collected	39250		
Independent reflections	9395 [<i>R</i> (int) = 0.0280]	9395 [<i>R</i> (int) = 0.0280]	
Completeness to theta = 25.000°	99.8 %	99.8 %	
Absorption correction	Semi-empirical from e	Semi-empirical from equivalents	
Max. and min. transmission	0.8012 and 0.7368	0.8012 and 0.7368	
Refinement method	Full-matrix least-squa	Full-matrix least-squares on F ²	
Data / restraints / parameters	9395 / 0 / 714	9395 / 0 / 714	
Goodness-of-fit on F ²	1.057		
Final R indices [I>2sigma(I)]	<i>R</i> 1 = 0.0346, <i>wR</i> 2 = 0.	0766	
R indices (all data)	R1 = 0.0443, wR2 = 0.	<i>R</i> 1 = 0.0443, <i>wR</i> 2 = 0.0818	
Extinction coefficient	n/a		
Largest diff. peak and hole	t diff. peak and hole 0.602 and –0.896 e.Å ⁻³		

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