

Stereoselective Coordination of Ditopic Phosphohlyl-Azahelicenes: A Novel Approach Towards Structural Diversity in Chiral π -Conjugated Assemblies

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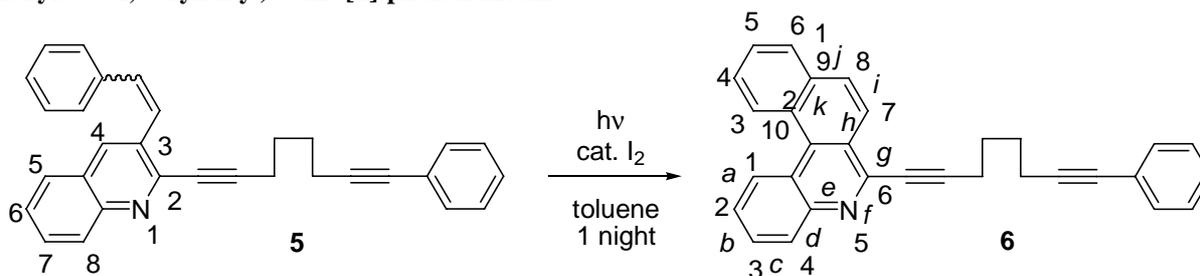
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Supporting information

Experimental Section

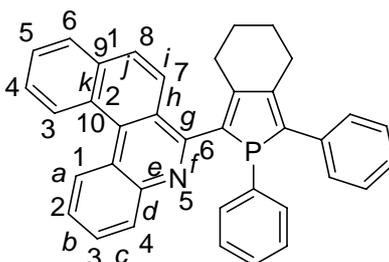
All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). PPhBr₂ was prepared as described in the literature.¹ Irradiation reactions were conducted using a Heraeus TQ 150 mercury vapor lamp. Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063-0.200 mm) in 3.5-20 cm columns. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker AM300 and DPX200. ¹H and ¹³C NMR chemical shifts were reported in parts per million (ppm) relative to Me₄Si as external standard. ³¹P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H₃PO₄ and were decoupled from the proton. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1.

6-(8-Phenyl-1,7-diyn-1-yl)-benzo[k]-phenanthridine **6**

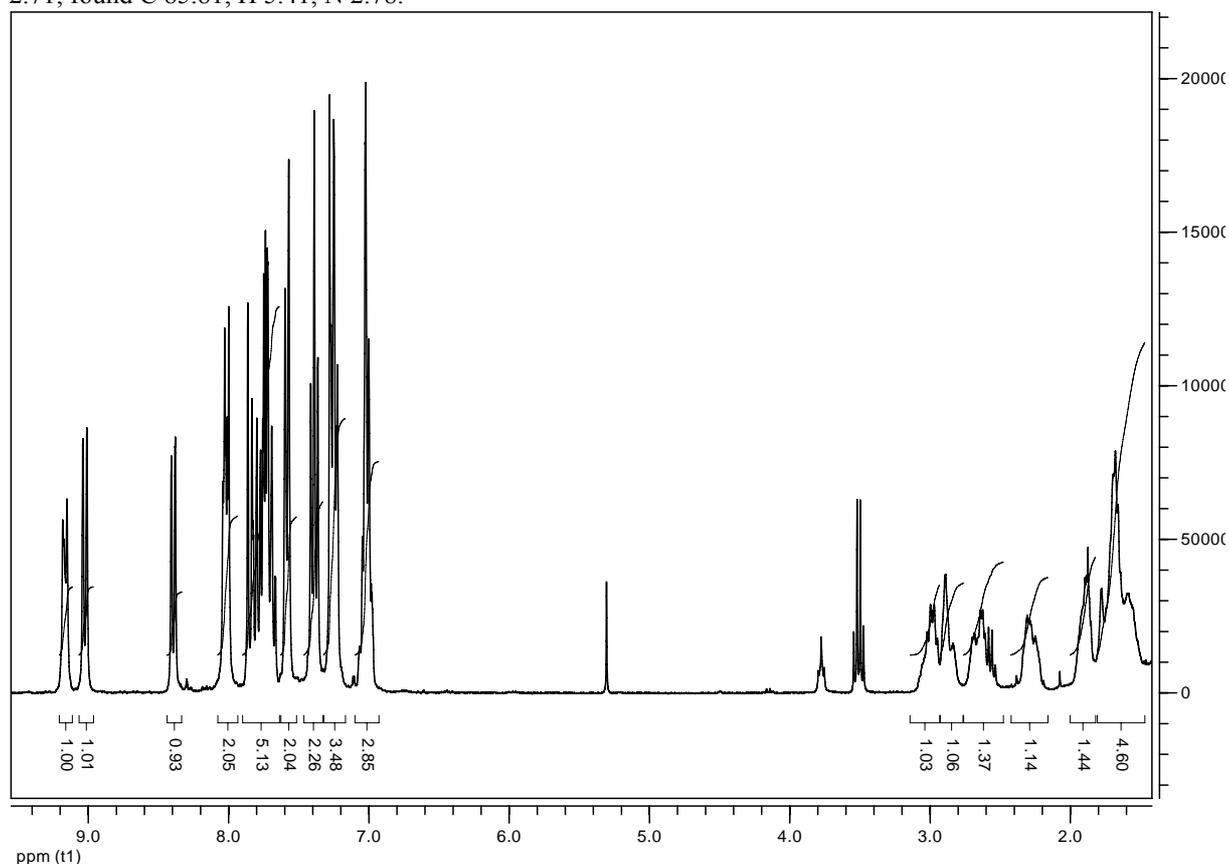


A toluene (250 mL) solution of quinoline **5** (150 mg, 0.36 mmol) containing catalytic amounts of iodine was irradiated for one night using a Heraeus TQ 150 mercury vapour lamp. Evaporation of the solvent followed by purification by column chromatography over silica gel (using heptane / EtOAc 8:2 as eluent) afforded **6** (92 mg, 62%) as an orange oil. RF (hept/AcOEt 8:2) = 0.21. ¹H NMR (300 MHz, CDCl₃): δ 9.09 (m, 1H), 8.96 (d, $J=8.7$ Hz, 1H), 8.48 (d, $J=8.7$ Hz, 1H), 8.32 (dd, $J=8.3$ Hz, 1.5 Hz, 1H), 8.0 (m, 1H), 7.94 (d, $J=8.7$ Hz, 1H), 7.68-7.78 (m, 4H), 7.44-7.47 (m, 2H), 7.28-7.30 (m, 3H), 2.76 (t, $J=6.8$ Hz, 2H, \equiv CCH₂), 2.57 (t, $J=6.8$ Hz, 2H, \equiv CCH₂), 1.91-2.04 (m, 4H, \equiv CCH₂CH₂). ¹³C NMR (75 MHz, CDCl₃): 146.0 (C), 144.4 (C), 135.0 (C), 131.6 (CH₂), 131.5 (C), 129.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH₂), 127.9 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH₂), 125.7 (C), 124.4 (CH), 124.0 (C), 123.9 (C), 95.5 and 89.7 (C \equiv CCH₂), 81.2 and 79.6 (C \equiv CCH₂), 28.1 and 27.6 (C \equiv CCH₂), 19.5 and 19.1 (C \equiv CCH₂CH₂). HRMS (EI), calcd. for C₃₁H₂₃N: 409.18305; found: 409.1837. UV/vis (CH₂Cl₂): 284 (46400), 315 (14400), 335 (5100), 351 (2700), 369 (3600), 388 (2700), 425 (700).

1-Phenyl-2-(benzo[k]-phenanthrid-6-yl)-5-phenyl-3,4butano-phosphole **2b**

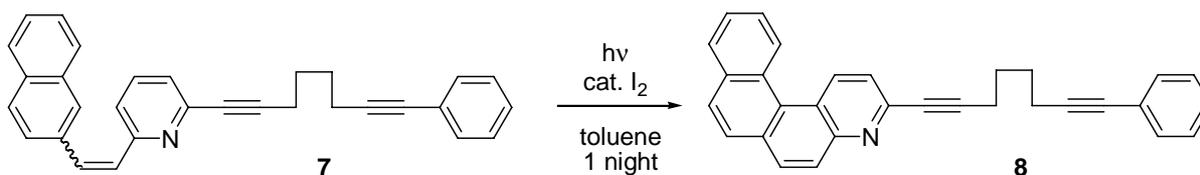


To a THF solution (10 mL) of diyne **6** (113 mg, 0.28 mmol) and Cp_2ZrCl_2 (81 mg, 0.28 mmol) under argon was added dropwise, at -78°C , $n\text{-BuLi}$ 1.6 M in hexanes (0.4 mL, 0.66 mmol). The reaction mixture was warmed to room temperature and stirred for one night. To this solution was added, at -50°C , freshly distilled PhPBr_2 (63 μL , 0.3 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 30 hours. The mixture was then filtered over basic alumina (using THF as eluent) under inert atmosphere and the volatiles were removed *in vacuo*. A final purification by column chromatography over silica gel (using heptane / EtOAc 8:2 as eluent) afforded the phosphole **2b** (65 mg, 45%) as a yellow solid. Mp 179°C . RF (heptane / AcOEt 8:2) 0.2. ^{31}P NMR (81 MHz, CDCl_3): δ 20.7 ppm. ^1H NMR (300 MHz, CDCl_3): δ 9.2 (m, 1H), 9.03 (d, $J=8$ Hz, 1H), 8.38 (d, $J=7.7$ Hz, 1H), 8.02 (m, 2H), 7.66-7.87 (m, 5H), 7.58 (bd, $J=8$ Hz, 2H), 7.39 (bt, $J=7.3$ Hz, 2H), 7.26 (m, 3H), 7.02 (m, 3H), 2.95 (m, 2H), 2.65 (m, 1H), 2.25 (m, 1H), 1.85 (m, 2H), 1.65 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) (J(P,C) coupling constants not assigned): δ 157.4 (C), 157.2 (C), 156.9, 148.6 (C), 148.4 (C), 146.2 (C), 145.0 (C), 143.6 (C), 143.5 (C), 141.9 (C), 137.3 (C), 137.1 (C), 134.7 (C), 133.2 (CH), 132.9 (CH), 132.0 (C), 131.6 (C), 131.4 (C), 130.3 (CH), 129.3 (CH), 129.2 (CH), 129.1 (C), 128.7 (CH_{x2}), 128.6 (CH), 128.4 (CH_{x2}), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 126.9 (CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 125.0 (C), 124.9 (C), 124.4 (C_{x2}), 123.6 (C), 28.1 (CH_{2x2}), 23.3 (CH₂), 22.3 (CH₂). HRMS (EI), calcd. for $\text{C}_{37}\text{H}_{28}\text{NP}$: 517.19594; found: 517.1950. UV/vis (CH_2Cl_2): 278 (34200), 317 (12700), 336 (5800), 361 (5400), 379 (4900). Elemental Analysis (%) for $\text{C}_{37}\text{H}_{28}\text{NP}$: calcd C 85.86, H 5.45, N 2.71; found C 85.81, H 5.41, N 2.78.



300 MHz NMR spectrum in CDCl_3 of phosphole **2b**.

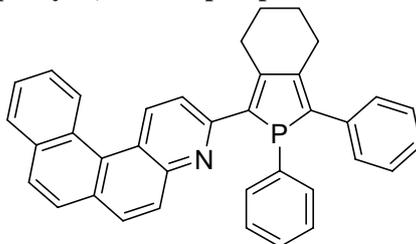
2-(8-Phenylocta-1,7-diyne-1-yl)-naphto[1,2-f]-quinoline **8**



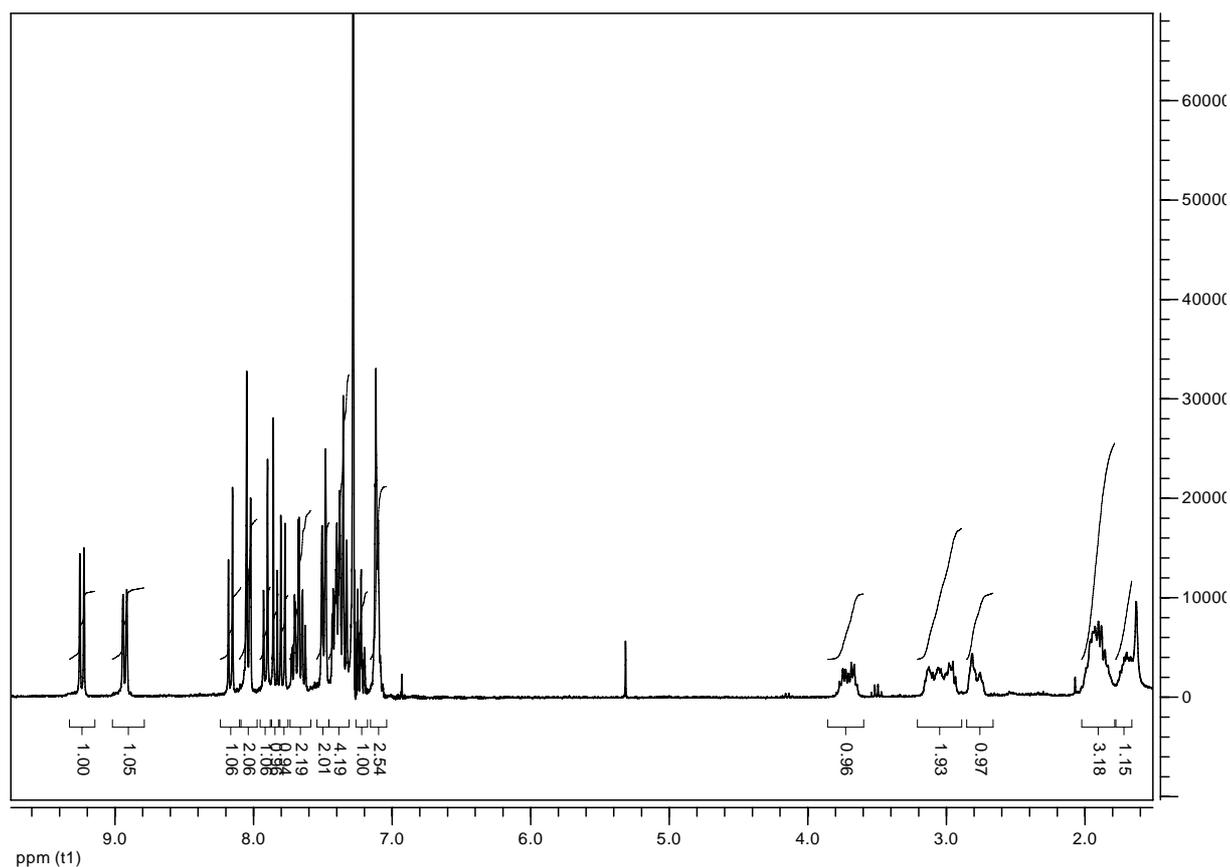
A toluene solution (570 mL) of substituted pyridine **7** (649 mg, 1.58 mmol) containing catalytic amounts of iodine was irradiated for one night using a Heraeus TQ 150 mercury vapour lamp. Evaporation of the solvent followed by purification by column chromatography over silica gel (using heptane / EtOAc 8:2 as eluent) afforded **8** (304 mg, 47%) as a beige solid. Mp

104 °C. RF (heptane / AcOEt 8:2) = 0.4. ¹H NMR (300 MHz, CDCl₃): δ 9.17 (d, *J*=8.8 Hz, 1H), 8.76 (d, *J*=7.4 Hz, 1H), 8.12 (d, *J*=8.8 Hz, 1H), 7.98 (d, *J*=8.9 Hz, 2H), 7.86 (d, *J*=8.5 Hz, 1H), 7.75 (d, *J*=8.6 Hz, 1H), 7.56-7.64 (m, 3H), 7.45-7.48 (m, 2H), 7.28-7.31 (m, 3H), 2.64 (t, *J*=6.6 Hz, 2H, ≡CCH₂), 2.54 (t, *J*=6.6 Hz, 2H, ≡CCH₂), 1.82-1.98 (m, 4H, ≡CCH₂CH₂). ¹³C NMR (75 MHz, CDCl₃): 148.7 (C), 142.6 (C), 135.4 (CH), 133.5 (C), 131.6 (CH₂), 131.1 (CH), 131.0 (C), 129.9 (C), 128.8 (CH), 128.4 (CH), 128.3 (CH₃), 127.5 (CH), 127.2 (CH), 126.7 (CH), 126.6 (CH), 126.5 (C), 126.3 (CH), 124.1 (C), 124.0 (C), 123.5 (CH), 91.8 and 89.8 (C≡CCH₂), 81.3 and 81.1 (C≡CCH₂), 28.1 and 27.6 (C≡CCH₂), 19.2 and 19.1 (C≡CCH₂ CH₂). HRMS (EI), calcd. for C₃₁H₂₃N: 409.18305; found: 409.1837. UV/vis (CH₂Cl₂): 289 (33700), 307 (14100), 324 (7700), 340 (6000), 363 (3000), 382 (3300).

1-Phenyl-2-(naphto[1,2-f]-quinol-2-yl)-5-phenyl-3,4butano-phosphole 2a

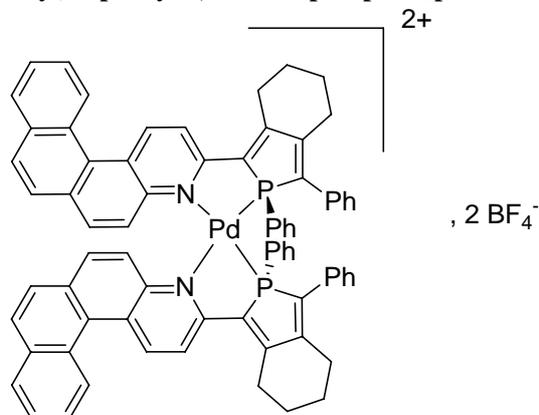


To a THF solution (10 mL) of diyne **8** (96 mg, 0.23 mmol) and Cp₂ZrCl₂ (69 mg, 0.23 mmol) under argon was added dropwise, at -78°C, n-BuLi 1.4 M in hexanes (0.4 mL, 0.56 mmol). The reaction mixture was warmed to room temperature and stirred for one night. To this solution was added, at -50°C, freshly distilled PhPBr₂ (53 μL, 0.26 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 30 hours. The mixture was then filtered over basic alumina (using THF as eluent) under inert atmosphere and the volatiles were removed *in vacuo*. A final purification by column chromatography over silica gel (using heptane / EtOAc 8:2 as eluent) afforded the phosphole **2a** (76 mg, 63%) as a yellow solid. Single crystals were grown by slow evaporation of pentane in a chloroform solution. Mp 205 °C. RF (heptane / AcOEt 8:2) = 0.3. ³¹P NMR (81 MHz, CDCl₃): δ 12.2 ppm. ¹H NMR (300 MHz, CDCl₃): δ 9.23 (d, *J*=8.9 Hz, 1H), 8.92 (d, *J*=8 Hz, 1H), 8.16 (d, *J*=8.7 Hz, 1H), 8.03 (d, *J*=8.7 Hz, 2H), 7.9 (d, *J*=8.7 Hz, 1H), 7.86 (d, *J*=8.7 Hz, 1H), 7.78 (d, *J*=8.7 Hz, 1H), 7.66 (m, 2H), 7.49 (d, *J*=7.8 Hz, 2H), 7.32-7.40 (m, 4H), 7.08-7.22 (m, 1H), 6.96 (m, 3H), 3.66-3.74 (m, 1H), 2.95-3.12 (m, 2H), 2.79 (m, 1H), 1.6-1.95 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) (J(P,C) coupling constants not assigned): δ 155.4 (C), 155.1 (C), 154.8 (C), 149.8 (C), 149.7 (C), 146.3 (C₂), 144.7 (C), 144.6 (C), 137.0 (C), 135.2 (CH), 133.7 (CH), 133.5 (CH), 132.3 (C), 132.2 (C), 130.5 (CH), 130.4 (C), 130.1 (C), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH₂), 127.6 (CH), 127.5 (CH), 127.0, 126.8 (CH), 126.4 (CH₂), 126.1 (CH), 123.0 (C₂), 121.1 (CH), 121.0 (CH), 29.7 (CH₂), 29.2 (CH₂), 28.2 (CH₂), 23.3 (CH₂). HRMS (EI), calcd. for C₃₇H₂₈NP: 517.19594; found: 517.1942. UV/Vis (CH₂Cl₂): 284 (49000), 320 (17000), 332 (14300), 382 (22800), 406 (28800). Elemental Analysis (%) for C₃₇H₂₈NP: calcd C 85.86, H 5.45, N 2.71; found C 85.85, H 5.44, N 2.73.

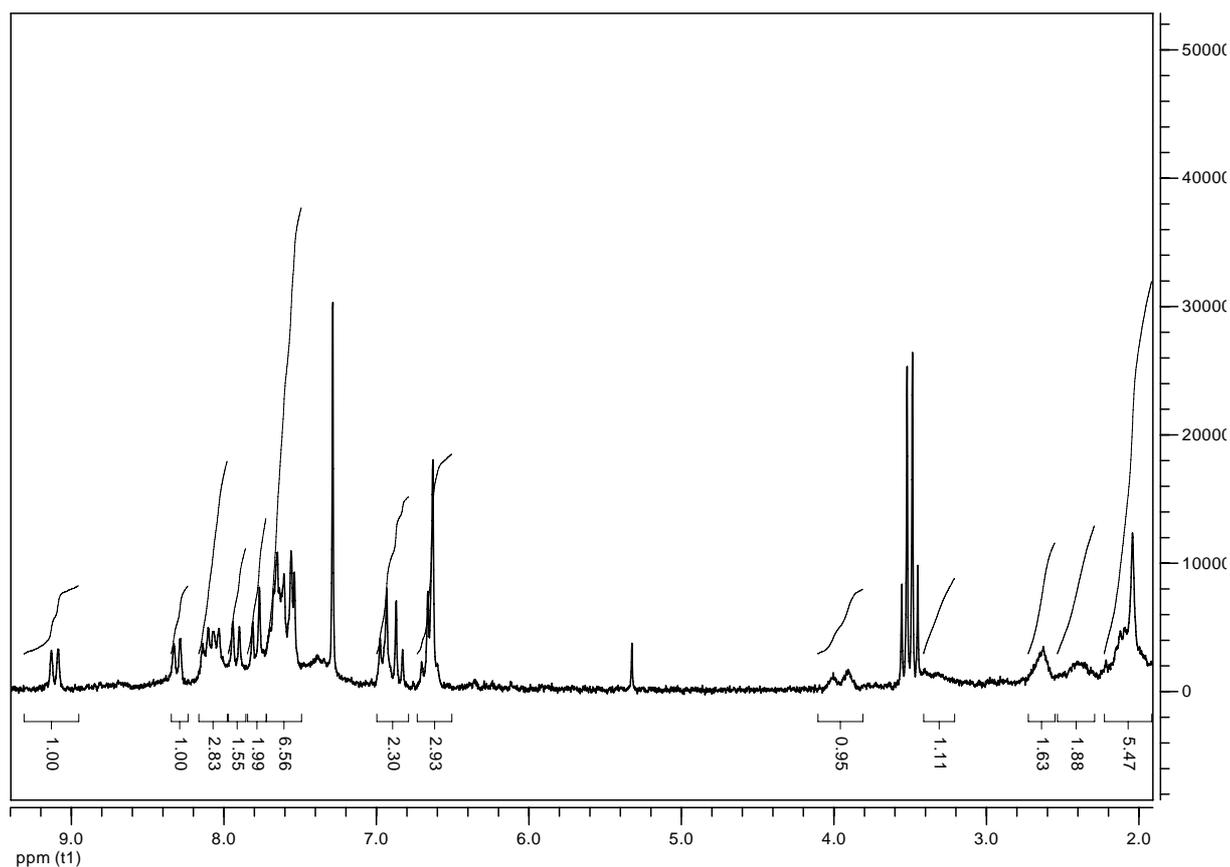


300 MHz NMR spectrum in CDCl_3 of phosphole **2a**.

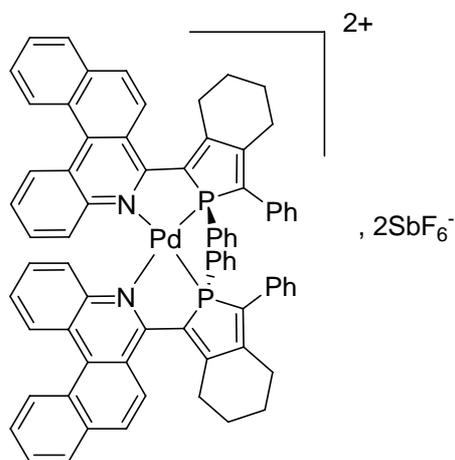
Bis[1-phenyl-2-(naphto[1,2-f]-quinol-2-yl)-5-phenyl-3,4butano-phosphole]palladium(II)- 2BF_4^- (3a**, 2BF_4^-).**



To a solution of phosphole **2a** (90 mg, 1.74 mmol) in dry CH_2Cl_2 (5 mL) under argon was added $\text{Pd}^{\text{II}}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ (39 mg, 0.87 mmol). After stirring at room temperature under argon for 1 hour, the solvent was stripped off and the precipitate was washed with dry Et_2O , yielding **3a**, 2BF_4^- (70 mg, 61%) as a dark red solid. Single crystals were grown by slow evaporation of pentane vapours into a CH_2Cl_2 solution but they were too small for X-ray analysis. ^{31}P NMR (81 MHz, CDCl_3): δ 76.7 ppm. ^1H NMR (200 MHz, CDCl_3): δ 9.11 (d, $J=8.9$ Hz, 1H), 8.3 (d, $J=8.7$ Hz, 1H), 8.03-8.14 (m, 2H), 7.9 (d, $J=8.6$ Hz, 1H), 7.79 (m, 2H), 7.28-7.65 (m, 7H), 6.83-6.97 (m, 3H), 6.66 (m, 3H), 3.95 (m, 1H), 3.30 (m, 1H), 2.63 (m, 2H), 2.41 (m, 2H), 2.04-12.12 (m, 4H). HRMS (ES), calcd. for $\text{C}_{74}\text{H}_{56}\text{N}_2^{35}\text{ClP}_2^{106}\text{Pd} ([\text{C}^{++}, \text{Cl}^-]^+)$: 1175.26420; found: 1175.2674. UV/Vis (CH_2Cl_2): 280 (39400), 303 (32400), 320 (25800), 340 (17300), 399 (11600), 525 (1400).

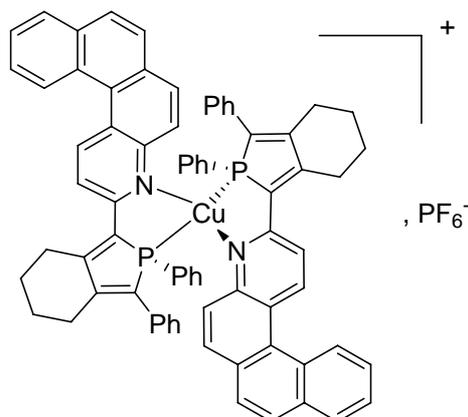


Bis[1-phenyl-2-(benzo[k]-phenanthrid-6-yl)-5-phenyl-3,4butano-phosphole]palladium(II)-2SbF₆⁻ (3b**, 2SbF₆⁻).**



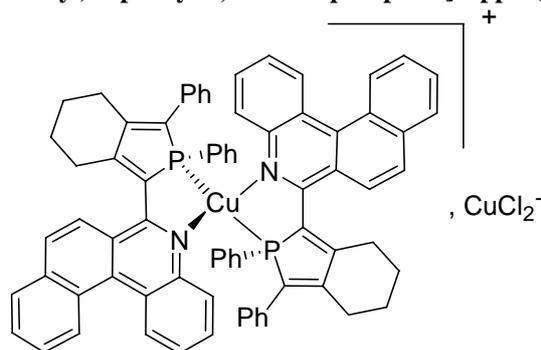
To a solution of phosphole **2b** (25 mg, 48 μmol) in dry CH₂Cl₂ (2 mL) under argon was added Pd^{II}(CH₃CN)₄(SbF₆)₂ (12 mg, 24 μmol). After stirring at room temperature under argon for 1 hour, the solvent was stripped off and the precipitate was washed with dry Et₂O, yielding **3b**, 2SbF₆⁻ (28 mg, 85%) as a dark red solid. Single crystals suitable for X-ray analysis were grown by slow evaporation of pentane vapours into a CH₂Cl₂ solution. ³¹P NMR (81 MHz, CD₂Cl₂): δ 81.6 ppm. HRMS (ES), calcd. for C₇₄H₅₆N₂³⁵ClP₂¹⁰⁶Pd ([C⁺⁺, Cl⁻]⁺): 1175.26420; found: 1175.2710. UV/Vis (CH₂Cl₂): 284 (98900), 313 (57500), 402 (15400), 500 (3400).

Bis[1-phenyl-2-(naphtho[1,2-f]-quinol-2-yl)-5-phenyl-3,4butano-phosphole] copper(I)-PF₆⁻ (4a**,PF₆⁻).**

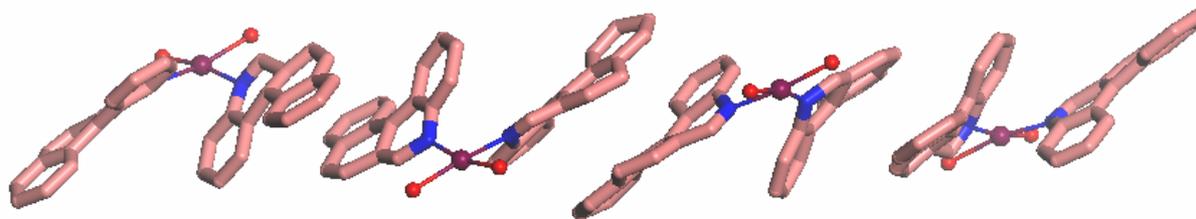


To a solution of phosphole **2a** (30 mg, 0.56 mmol) in dry CH₂Cl₂ (5 mL) under argon was added Cu^I(CH₃CN)₄(PF₆) (10 mg, 0.28 mmol). After stirring at room temperature under argon for 1 hour, the solvent was stripped off and the precipitate was washed with dry Et₂O, yielding **4a**,PF₆⁻ (49 mg, 77%) as a yellow solid. Single crystals were grown by slow evaporation of pentane vapours into a CH₂Cl₂ solution. ³¹P NMR (81 MHz, CDCl₃): δ 5-6 ppm. UV/Vis (CH₂Cl₂): 292 (44400), 342 (20400), 384 (16600), 403 (17400).

Bis[1-phenyl-2-(benzo[k]-phenanthrid-6-yl)-5-phenyl-3,4butano-phosphole]copper(I)-CuCl₂⁻ (4b**,CuCl₂⁻).**



To a solution of phosphole **2b** (20 mg, 39 μmol) in dry CH₂Cl₂ (2 mL) under argon was added Cu^ICl (2 mg, 20 μmol). After stirring at room temperature under argon for 1 hour, the solvent was stripped off and the precipitate was washed with dry Et₂O, yielding **4b**,CuCl₂⁻ (18 mg, 82%) as a bright yellow solid. Single crystals suitable for X-ray analysis were grown by slow evaporation of pentane vapours into a CH₂Cl₂ solution. ³¹P NMR (81 MHz, CDCl₃): δ 5-6 ppm. UV/Vis (CH₂Cl₂): 278 (71400), 322 (45200), 368 (29900), 403 (24800).



Simplified view showing the packing of **3b** (phenyls, H atoms, have been omitted for clarity).

X-ray Crystallographic Study

Single crystals suitable for X-Ray crystal analysis were obtained by slow diffusion of pentane vapours into a dichloromethane solution of **2a**, **3b** and **4a,b** at room temperature. Crystals were removed from their mother solution, coated with oil and rapidly transferred to the diffractometer in order to prevent potential solvent evaporation. Single crystal data collections were performed at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Reflections were indexed, Lorentz-polarization corrected and integrated by the SAINT program² included in the APEX2 software package. The data merging process was performed using the SCALEPACK program.³ Structure determinations were performed by direct methods with the solving program SIR97,⁴ that revealed all the non hydrogen atoms. SHELXL program⁵ was used to refine the structures by full-matrix least-squares based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. In all the crystal lattices of the coordination complexes, CH₂Cl₂ molecules were found in addition to the counter-anions. Some of these solvent molecules as well as the counter-anions were found to be highly disordered, leading to rather high anisotropic displacement parameters for some atoms. As a consequence, final agreement (R) factors were modest in some cases. Nevertheless, in case of the Cu^I complexes **4a,b**, anisotropic displacement parameters associated to the atoms of the cationic coordination complexes are always satisfactory, allowing a primarily assignment of these modest R factors to an inadequate modelling of the disordered CH₂Cl₂ molecules or counter-anions. In the case of the Pd^{II} complex **3b**, the crystals recovered were always characterized by small dimensions and were weakly diffracting. In addition, these crystals lose quickly their included solvent molecules and exhibit large crystal cell parameter ($c = 81.28(2) \text{ \AA}$). Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.⁶ CCDC reference numbers CCDC 651119 – 651122 contain the supplementary crystallographic data for **2a**, **4b**, **4a** and **3b**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystallographic data :

Crystal data **2a**: C₃₇H₂₈NP, $M_r = 517.57$, $0.2 \times 0.05 \times 0.03 \text{ mm}^3$, triclinic, $P \bar{1}$, $a = 9.5107(4)$, $b = 10.9272(5)$, $c = 14.1036(6) \text{ \AA}$, $\alpha = 72.146(3)^\circ$, $\beta = 70.845(3)^\circ$, $\gamma = 84.199(3)^\circ$, $V = 1317.89(10) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 1.304 \text{ g cm}^{-3}$, $\mu = 0.132 \text{ mm}^{-1}$, $F(000) = 544$, 18731 reflections were collected in the range $5.24 \leq \theta \leq 24.71^\circ$ of which 4428 were unique, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $R_{\text{int}} = 0.0539$, 352 parameters, $R1(F_0) = 0.0393$, $\omega R2(F_0^2) = 0.0795$ and GOF = 1.022 for $I \geq 2\sigma(I)$ ($R1(F_0) = 0.0659$, $\omega R2(F_0^2) = 0.0905$ for all data), max/min residual density 0.394/-0.387 e. \AA^{-3} .

Crystal data **3b**.2SbF₆: C_{75.5}H₅₉Cl₃PdN₂P₂F₁₂Sb₂, $M_r = 1740.44$, $0.2 \times 0.1 \times 0.05 \text{ mm}^3$, Tetragonal, $I4_1/a$, $a = 18.695(5)$, $b = 18.695(5)$, $c = 81.28(2) \text{ \AA}$, $V = 28408(11) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 16$, $\rho_{\text{calcd}} = 1.628 \text{ g cm}^{-3}$, $\mu = 1.240 \text{ mm}^{-1}$, $F(000) = 13808$, 86356 reflections were collected in the range $5.10 \leq \theta \leq 23.25^\circ$ of which 10112 were unique, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $R_{\text{int}} = 0.2627$, 1022 parameters, $R1(F_0) = 0.1074$, $\omega R2(F_0^2) = 0.2213$ and GOF = 1.128 for $I \geq 2\sigma(I)$ ($R1(F_0) = 0.1827$, $\omega R2(F_0^2) = 0.2542$ for all data), max/min residual density 1.324/-1.249 e. \AA^{-3} .

Crystal data **4a**.PF₆: C_{76.5}H₆₁CuN₂P₆F₆Cl₅, $M_r = 1455.97$, $0.1 \times 0.1 \times 0.03 \text{ mm}^3$, triclinic, $P \bar{1}$, $a = 14.431(2)$, $b = 21.614(3)$, $c = 22.007(3) \text{ \AA}$, $\alpha = 82.315(4)^\circ$, $\beta = 85.456(5)^\circ$, $\gamma = 75.858(4)^\circ$, $V = 6588.7(16) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.468 \text{ g cm}^{-3}$, $\mu = 0.672 \text{ mm}^{-1}$, $F(000) = 2988$, 37977 reflections were collected in the range $5.10 \leq \theta \leq 23.26^\circ$ of which 18196 were unique, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $R_{\text{int}} = 0.0996$, 1914 parameters, $R1(F_0) = 0.0793$, $\omega R2(F_0^2) = 0.1887$ and GOF = 1.028 for $I \geq 2\sigma(I)$ ($R1(F_0) = 0.1628$, $\omega R2(F_0^2) = 0.2282$ for all data), max/min residual density 0.872/-0.911 e. \AA^{-3} .

Crystal data **4b**.CuCl₂: C₁₅₃H₁₂₂Cu₄N₄P₄Cl₁₄, $M_r = 2890.89$, $0.2 \times 0.2 \times 0.1 \text{ mm}^3$, monoclinic, $C2/c$, $a = 32.938(2)$, $b = 19.965(1)$, $c = 24.449(1) \text{ \AA}$, $\beta = 124.683(2)^\circ$, $V = 13221.0(12) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.452 \text{ g cm}^{-3}$, $\mu = 1.022 \text{ mm}^{-1}$, $F(000) = 5928$, 68081 reflections were collected in the range $5.11 \leq \theta \leq 26.37^\circ$ of which 13411 were unique, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $R_{\text{int}} = 0.0467$, 969 parameters, $R1(F_0) = 0.0485$, $\omega R2(F_0^2) = 0.1187$ and GOF = 1.028 for $I \geq 2\sigma(I)$ ($R1(F_0) = 0.0647$, $\omega R2(F_0^2) = 0.1302$ for all data), max/min residual density 1.580/-1.127 e. \AA^{-3} .

Scheme S1. General labelling scheme adopted for the ligands **2a** and **2b**.

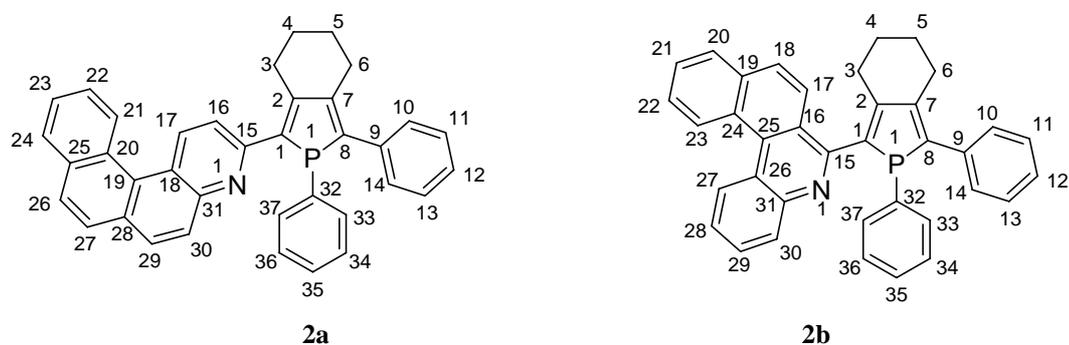


Figure S1 . Molecular structure of the ligand **2a** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

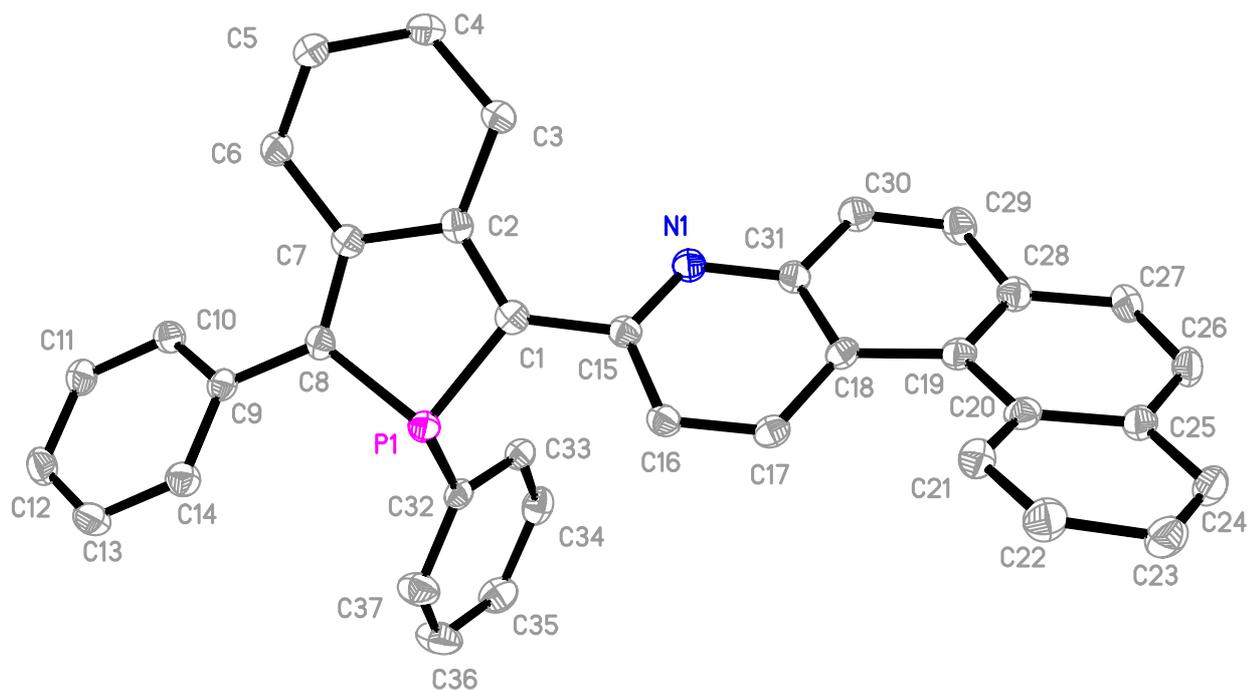


Figure S2. Molecular structure of the cation of **3b** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

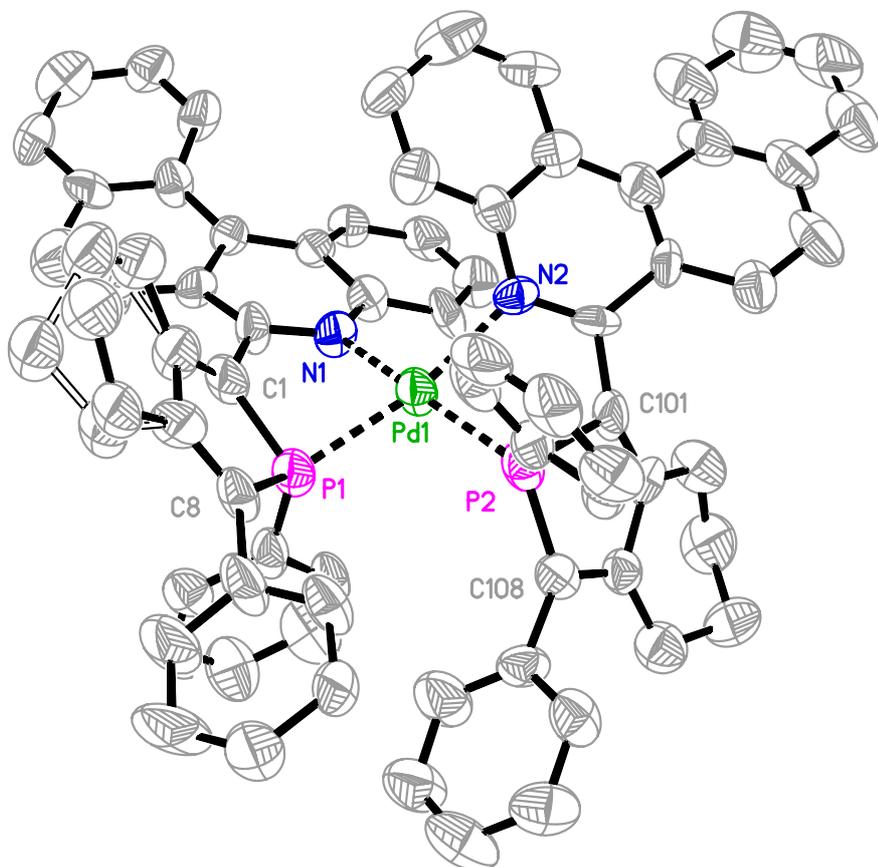


Figure S3. Molecular structure of two symmetrically independent complexes presents in the asymmetric unit of the derivative **4a** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

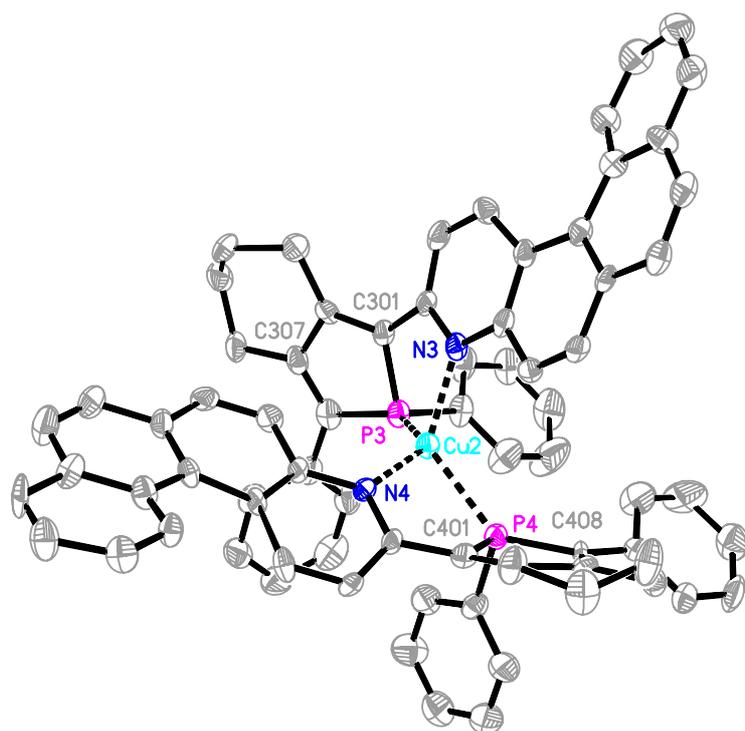
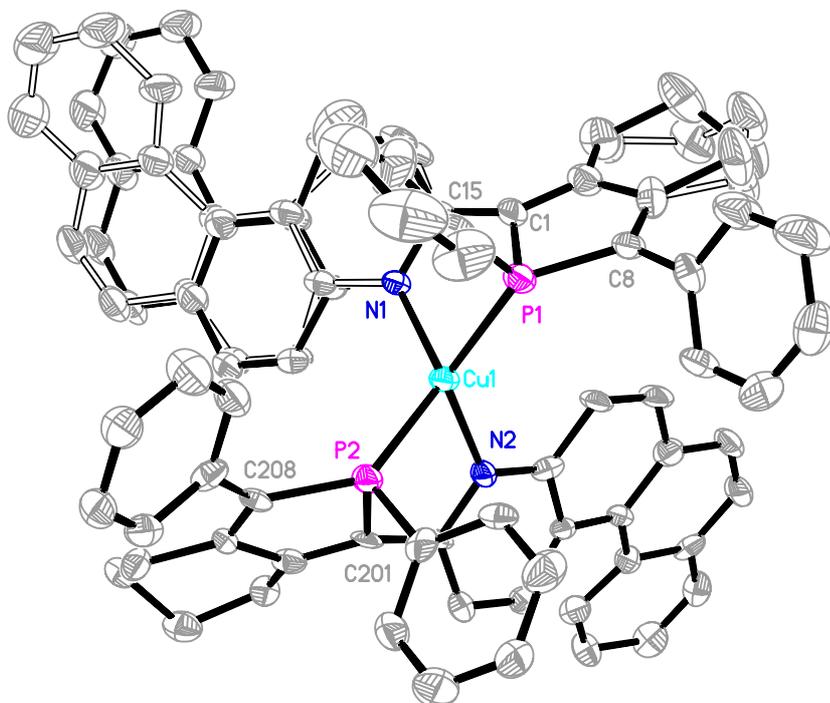
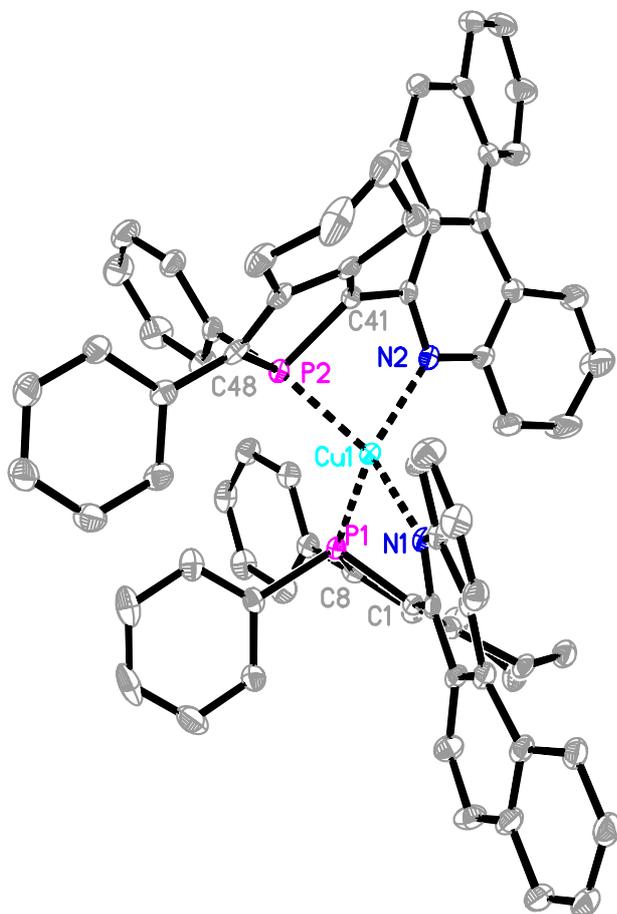


Figure S4. Molecular structure of the cationic complex present in the asymmetric unit of the derivative **4b** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



References for the Supporting Information

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