Neutral copper-phosphido-borane complexes: Synthesis, characterization, and use as precatalysts in Csp-P bond formation

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Supporting Information

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(I) General remarks

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Toluene, diethyl ether, dichloromethane and THF were purified by an Innovative Technology Pure Solv. Device (activated alumina column containing a copper catalyst and molecular sieves) and degassed. Chromatographic purifications were conducted using Merck silica gel Si 60 (40-63 µm) and TLC were performed on silica gel 60-F_{254} plates (0.1 mm) with UV or $KMnO_4$ detection. ^1H, ^{13}C, ^{31}P NMR spectra were recorded on a BRUKER AVANCE III 400 or 500 spectrometer. ^{11}B NMR spectrum was obtained on a 500 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm using the residual peak of chloroform-d (7.26 and 77.16 ppm) or dichloromethane-d_2 (5.32 and 53.84 ppm) as internal standard. ^{31}P and ^{11}B NMR chemical shifts are reported relative to respectively H_3PO_4 (85%) and $BF_3.Et_2O$ used as external references. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singulet, d = doublet, t = triplet, quint = quintuplet, sext = sextuplet, m = multiplet, br = broad. High Resolution Mass Spectrometry was performed on a Varian MAT 311 spectrometer. IR spectra were recorded on Spectrum One Perkin Elmer spectrometer and only the strongest or structurally most important peaks are listed.

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(II) Synthesis and characterization of complexes [R_2PHCuXphen]

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Complex [Ph_2PHCuIphen] (3a):
In a Schlenk tube, flushed with nitrogen, CuI (438 mg, 2.3 mmol, 1 equiv.), 1,10-phenanthroline (414 mg, 2.3 mmol, 1 equiv.) and diphenylphosphine (0.4 mL, 2.3 mmol, 1 equiv.) were dissolved in degassed dry dichloromethane (40 mL) at − 78°C. The reaction mixture was stirred at room temperature for 2 hours. After evaporation of the solvent, the solid residue was washed with diethyl ether (20 mL) and pentane (20 mL) affording an orange solid (1.2 g, 94% yield). Recrystallization at −20° C from $CHCl_3/Et_2O$ gave orange crystals. Mp = 150 °C (dec.)

^1H NMR (500 MHz, $CDCl_3$) δ 8.98 (br, 2 H), 8.34 (br, 2 H), 7.86 (br, 2 H), 7.68−7.61 (m, 6 H), 7.35−7.27 (m, 6 H), 6.02 (d, $^1J_{PH}$ = 312.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 143.4, 136.4, 133.8 (d, $^2J_{CP}$ = 10.9 Hz), 131.4 (d, $^1J_{CP}$ = 28.6 Hz), 129.6, 129.2, 128.8, 126.8, 124.7.

^{31}P NMR (202 MHz, $CDCl_3$) δ −32.2 (br).

IR (neat): 3041, 2308, 1508, 1480, 1435, 1422, 1141, 1095, 913, 842, 727, 693 cm^{-1}.

HRMS (ESI) Calcd for $C_{24}H_{19}N_2PCu$ [M−I]$^+$: 429.0582. Found: 429.0584.

Anal. Calcd for $C_{24}H_{19}CuIN_2P$: C, 51.77; H, 3.44; N, 5.03. Found: C, 51.87; H, 3.68; N, 5.04.

Crystallographic data of **complex [Ph₂PHCuIphen] (3a)**: Xcalibur-Saphire II Oxford Diffraction diffractometer ($Mo_{K\alpha}$ λ=0.71073 Å; graphite monochromator; T=140(2) K. Formula $C_{195.5}H_{155.5}Cl_{10.50}Cu_8I_8N_{16}P_8$, formula weight 4872.36, crystal system triclinic, space group P-1, crystal dimensions 0.18 x 0.11 x 0.02 mm³, a=17.7530(9), b=17.8081(7), c=34.955(2) Å, α=90.756(4), β=91.063(4), γ=119.895(5) °, V= 9575.7(8) Å³, Z=2, ρ_{calcd}=1.690 Mgm⁻³, μ=2.430 mm⁻¹, $2\theta_{max}$=54.00°, 65308 measured reflections, 7583 independent reflections (R_{int}= 0.1588), $R1$ [I>2σ(I)]=0.0869, $wR2$ [I>2σ(I)]= 0.1433, GOF=0.709, 1142 parameters, final difference map within 2.243 and -2.557 eÅ⁻³. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 826962 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): Cu1A-N1A 2.046(16), Cu1A-N2A 2.082(14), Cu1A-P1A 2.175(7), Cu1-I1A 2.634(3), N1A-Cu1A-N2A 81.9(6), N1A-Cu1A-P1A 130.7(4), N2A-Cu1A-P1A 118.4(5), N1A-Cu1A-I1A 99.3(4), N2A-Cu1A-I1A 108.2(4), P1A-Cu1A-I1A 113.38(18).
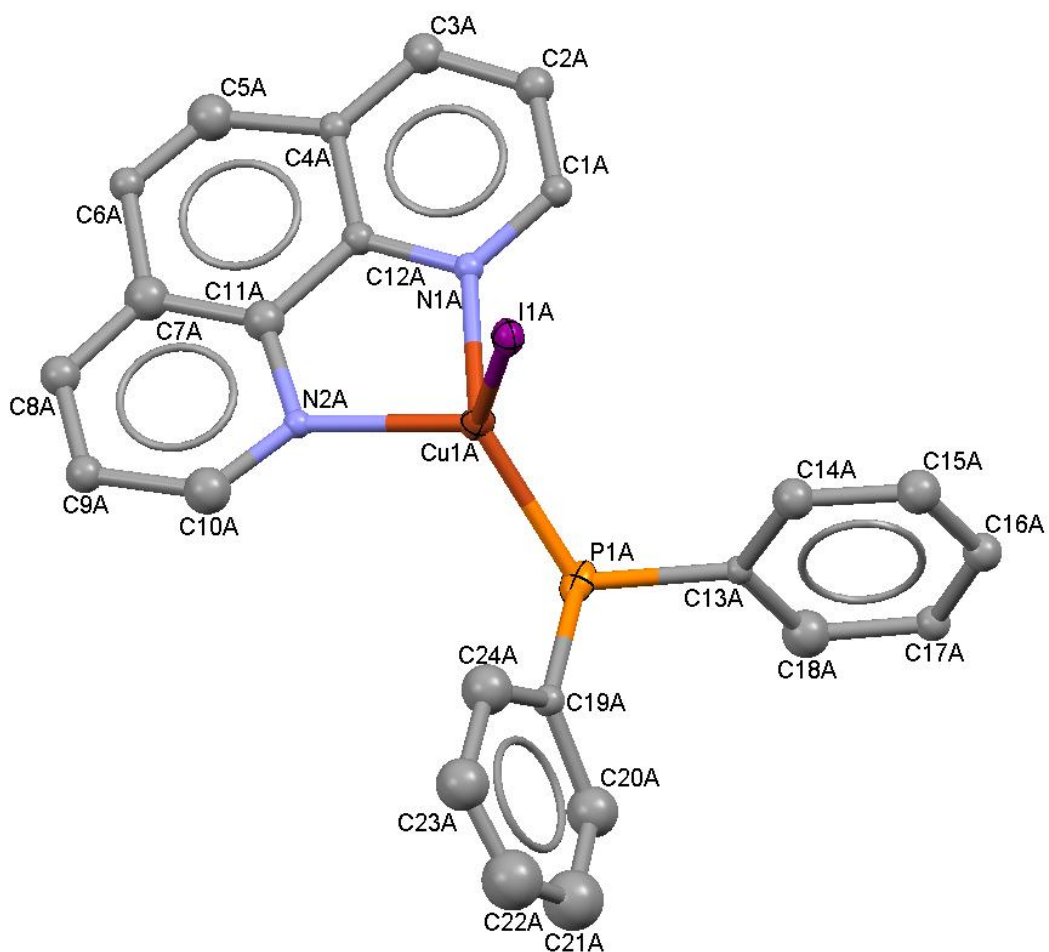
Complex [Et₂PHCuIphen] (3b):

In a Schlenk tube, flushed with nitrogen, CuI (343 mg, 1.8 mmol, 1 equiv.), 1,10-phenanthroline (324 mg, 1.8 mmol, 1 equiv.) and diethylphosphine (3 mL of a 10% in hexane, 2.1 mmol, 1.2 equiv.) were dissolved in degassed dry dichloromethane (25 mL) at −78 °C. The reaction mixture was stirred at room temperature for 2 hours. After evaporation of solvent, the solid residue was washed with diethyl ether (20 mL) and pentane (20 mL), affording an orange solid (0.70 g, 84% yield). Recrystallization at −20 °C from CH_2Cl_2 /Et₂O gave orange crystals. Mp = 155 °C (dec.)

^{1}H NMR (500 MHz, CD₂Cl₂) δ 9.15 (d, $^3J_{HH}$ = 3.9 Hz, 2 H), 8.40 (d, $^3J_{HH}$ = 7.9 Hz, 2 H), 7.89 (s, 2 H), 7.80–7.78 (m, 2 H), 3.92 (dquint, $^1J_{PH}$ = 287.4 Hz, $^3J_{HH}$ = 6.4 Hz, 1 H), 1.81–1.72 (m, 4 H), 1.13 (dt, $^3J_{HP}$ = 16.8 Hz, $^3J_{HH}$ = 7.5 Hz, 6 H).

^{13}C NMR (125 MHz, CD₂Cl₂) δ 149.8, 143.7, 136.7, 129.5, 127.0, 124.9, 14.4 (d, $^1J_{CP}$ = 19.8 Hz), 11.4 (d, $^2J_{CP}$ = 1.8 Hz).

^{31}P NMR (202 MHz, CD₂Cl₂) δ −40.9 (br).

IR (neat): 3044, 2959, 2318, 1621, 1582, 1508, 1423, 1135, 1054, 841, 727 cm^{-1}.

HRMS (ESI) Calcd for $C_{16}H_{19}N_2PCu$ [M−I]$^+$: 333.0582. Found: 333.0584.

Anal. Calcd for $C_{16}H_{19}CuIN_2P$: C, 41.71; H, 4.16; N, 6.08. Found: C, 41.86; H, 4.30; N, 6.20.

Crystallographic data of **Complex [Et₂PHCuIphen] (3b):** Bruker Kappa APEXII CCD diffractometer (Mo$_{Kα}$ λ=0.71073 Å; graphite monochromator; T=150(2) K. Formula $C_{16}H_{19}CuIN_2P$, formula weight 460.74, crystal system monoclinic, space group $P2(1)/n$, crystal dimensions 0.22 x 0.18 x 0.14 mm^3, a=7.6247(3), b=15.4479(5), c=14.7132(5) Å, α=90.00, β=91.854(2), γ=90.00°, V= 1732.10(11) Å^3, Z=4, $ρ_{calcd}$=1.767 Mgm^{-3}, μ=3.130 mm^{-1}, $2θ_{max}$=64.52°, 44076 measured reflections, 5254 independent reflections (R_{int}= 0.0284), $R1$ [I>2σ(I)]=0.0226, $wR2$ [I>2σ(I)]= 0.0519, GOF=1.096, 196 parameters, final difference map within 0.747 and -0.602 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 857695 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): Cu1-N1 2.0841(14), Cu1-N2 2.0771(15), Cu1-I1 2.6715(3), Cu1-P1 2.1833(5), P1-H1 1.29(3), N2-Cu1-N1 80.56(6), N2-Cu1-P1 131.99(5), N1-Cu1-P1 134.04(4), N2-Cu1-I1 103.21(4), N1-Cu1-I1 102.89(4), P1-Cu1-I1 99.375(14).
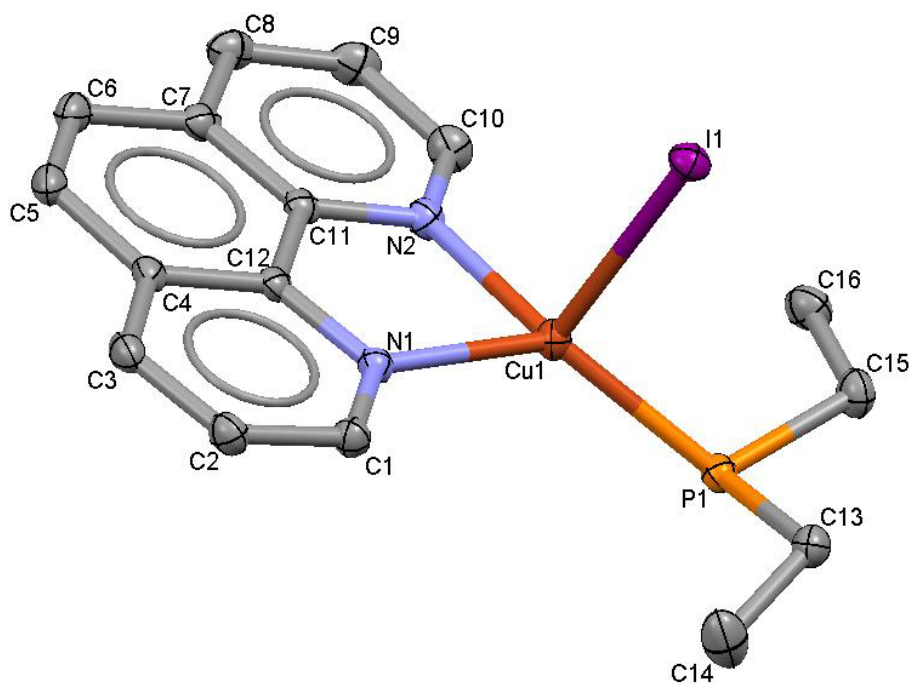
(III) Synthesis and characterization of complexes [R$_2$PHCuPPh$_2$BH$_3$phen]

Complex [Ph$_2$PHCuPPh$_2$BH$_3$phen] (4a):

Degassed dry dichloromethane (20 mL) was introduced at −78 °C into a Schlenk tube containing [Ph$_2$PHCuIphen] **(3a)** (300 mg, 0.54 mmol, 1 equiv.), Me$_3$SiOK (76 mg, 0.59 mmol, 1.1 equiv.) and diphenylphosphine-borane **(1)** (108 mg, 0.54 mmol, 1 equiv.). The reaction mixture was stirred for 3 hours. After elimination of KI by filtration, the solvent was removed under vacuum. The resulting red solid was washed with diethyl ether (5 mL) and pentane (5 mL) (279 mg, 82% yield). Single crystals of **4a** were obtained by recrystallization from a mixture of dichloromethane/diethyl ether at 0 °C. Mp = 152 °C (dec.)

^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 8.85 (br s, 2 H), 8.32 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.9 Hz, 2 H), 7.85 (s, 2 H), 7.67−7.65 (m, 2 H), 7.34−7.27 (m, 10 H), 7.21−7.18 (m, 4 H), 6.97−6.92 (m, 6 H), 5.96 (d, $^1J_{PH}$ = 307.4 Hz, 1 H), 1.31−0.78 (m, 3 H).

^{13}C NMR (125 MHz, CD$_2$Cl$_2$) δ 150.1, 143.8, 143.8 (d, $^1J_{CP}$ = 16.1 Hz), 136.3, 133.7 (d, $^2J_{CP}$ = 13.9 Hz), 133.3 (d, $^2J_{CP}$ = 10.5 Hz), 131.7 (d, $^1J_{CP}$ = 25.6 Hz), 129.7, 129.4, 128.9 (d, $^3J_{CP}$ = 8.6 Hz), 127.4 (d, $^3J_{CP}$ = 7.3 Hz), 127.0, 126.4, 124.6.

^{31}P NMR (202 MHz, CD$_2$Cl$_2$) δ −20.5 (br), −32.6 (br d, $^1J_{PH}$ = 307.4 Hz).

^{11}B NMR (160 MHz, CD$_2$Cl$_2$) δ −32.3 to −32.9 (m).

IR (neat): 3064, 2307, 1622, 1581, 1478, 1434, 1423, 1135, 1097, 1055, 838, 820, 736, 724, 693 cm^{-1}.

MS (ES$^+$) m/z 615 [M – BH$_3$ + H]$^+$.

Anal. Calcd for C$_{36}$H$_{32}$BCuN$_2$P$_2$: C, 68.75; H, 5.13; N, 4.45. Found: C, 68.40; H, 5.13; N, 4.56.

Crystallographic data of **complex [Ph$_2$PHCuPPh$_2$BH$_3$phen] (4a)**: Bruker Kappa APEXII CCD diffractometer (Mo$_{K\alpha}$ λ=0.71073 Å; graphite monochromator; T=291(2) K. Formula C$_{36}$H$_{32}$BCuN$_2$P$_2$, formula weight 628.93, crystal system triclinic, space group P-1, crystal dimensions 0.17 x 0.13 x 0.09 mm^3, a=9.7656(14), b=11.5098(17), c=16.082(3) Å, α=98.116(3), β=99.785(3), γ=112.221(4) °, V= 1606.7(4) Å^3, Z=2, ρ_{calcd}=1.300 Mgm^{-3}, μ=0.807 mm^{-1}, $2\theta_{max}$=58.28°, 30590 measured reflections, 6931 independent reflections (R_{int}= 0.0179), R1 [I>2σ(I)]=0.0330, wR2 [I>2σ(I)]= 0.0900, GOF=1.023, 384 parameters, final difference map within 0.614 and -0.243 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 857696 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): Cu1-N1 2.1439(13), Cu1-N2 2.0711(13), Cu1-P1 2.2427(5), Cu1-P2 2.2640(5), P2-B1 1.9480(19), N2-Cu1-N1 79.17(5), N2-Cu1-P1 114.27(4), N1-Cu1-P1 101.08(4), N2-Cu1-P2 118.20(4), N1-Cu1-P2 112.98(4), P1-Cu1-P2 121.105(19).
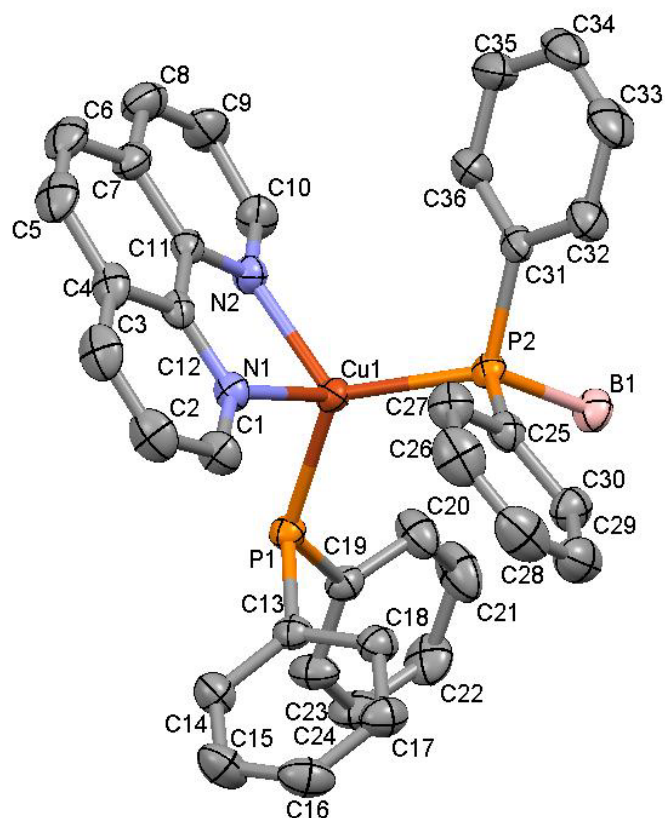
Complex [Et₂PHCuPPh₂BH₃phen] (4b):

Degassed dry dichloromethane (30 mL) was introduced at −78 °C into a Schlenk tube containing [Et₂PHCuIphen] (**3b**) (400 mg, 0.87 mmol, 1 equiv.), Me₃SiOK (123 mg, 0.96 mmol, 1.1 equiv.) and diphenylphosphine-borane (174 mg, 0.87 mmol, 1 equiv.). The reaction mixture was stirred for 3 hours. After elimination of KI by filtration, the solvent was removed under vacuum. The resulting red solid was washed with diethyl ether (10 mL) and pentane (10 mL) (414 mg, 89% yield). Single crystals of **4b** were obtained by recrystallization from a mixture of dichloromethane/pentane at 0°C. Mp = 122 °C (dec.)

^{1}H NMR (500 MHz, CD₂Cl₂) δ 9.10 (d, $^3J_{HH}$ = 3.8 Hz, 2 H), 8.32 (d, $^3J_{HH}$ = 7.8 Hz, 2 H), 7.83 (s, 2 H), 7.75–7.72 (m, 2 H), 7.32–7.28 (m, 4 H), 6.97–6.96 (m, 6 H), 3.90 (dquint, $^1J_{HP}$ = 283.1 Hz, $^3J_{HH}$ = 6.2 Hz, 1 H), 1.67–1.56 (m, 4 H), 1.00 (dt, $^3J_{HP}$ = 16.1 Hz, $^3J_{HH}$ = 7.5 Hz, 6 H), 1.28−0.76 (m, 3H).

^{13}C NMR (125 MHz, CD₂Cl₂) δ 149.8, 144.4 (d, $^1J_{CP}$ = 15.1 Hz), 143.8, 136.1, 133.2 (d, $^2J_{CP}$ = 10.5 Hz), 129.4, 127.3 (d, $^3J_{CP}$ = 7.2 Hz), 127.0, 126.1, 124.5, 14.1 (d, $^1J_{CP}$ = 17.0 Hz), 11.4.

^{31}P NMR (202 MHz, CD₂Cl₂) δ −21.3 (br), −42.8 (br).

^{11}B NMR (160 MHz, CD₂Cl₂) δ −32.4 to −33.0 (m).

IR (neat): 3047, 2962, 2318, 1621, 1582, 1475, 1423, 1135, 1095, 1054, 840, 727, 698 cm^{-1}.

HRMS (ESI) Calcd for C₁₆H₁₉N₂PCu [M−Ph₂PBH₃]$^+$: 333.0582. Found: 333.0585.

Anal. Calcd for $C_{28}H_{32}BCuN_2P_2$: C, 63.11; H, 6.05; N, 5.26. Found: C, 62.75; H, 6.12; N, 5.35.

Crystallographic data of **complex [Et₂PHCuPPh₂BH₃phen] (4b)**: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ=0.71073 Å; graphite monochromator; T=150(2) K. Formula $C_{28}H_{32}BCuN_2P_2$, formula weight 532.85, crystal system monoclinic, space group $C2/c$, crystal dimensions 0.32 x 0.28 x 0.21 mm^3, a=27.1263(5), b=13.9139(3), c=16.8585(3) Å, α=90.00, β=114.852(1), γ=90.00 °, V= 5773.71(19) Å^3, Z=8, ρ_{calcd}=1.226 Mgm^{-3}, μ=0.885 mm^{-1}, $2\theta_{max}$=56.58°, 44477 measured reflections, 5932 independent reflections (R_{int}= 0.0259), $R1$ [I>2σ(I)]=0.0507, $wR2$ [I>2σ(I)]= 0.1553, GOF=1.131, 314 parameters, final difference map within 1.353 and -0.626 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 857697 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): Cu1-N1 2.098(2), Cu1-N2 2.095(2), Cu1-P1 2.2505(8), Cu1-P2 2.2609(6), P2-B1 1.941(3), N2-Cu1-N1 79.86(9), N2-Cu1-P1 111.07(7), N1-Cu1-P1 107.02(6), N2-Cu1-P2 109.05(6), N1-Cu1-P2 127.73(6), P1-Cu1-P2 115.93(3).
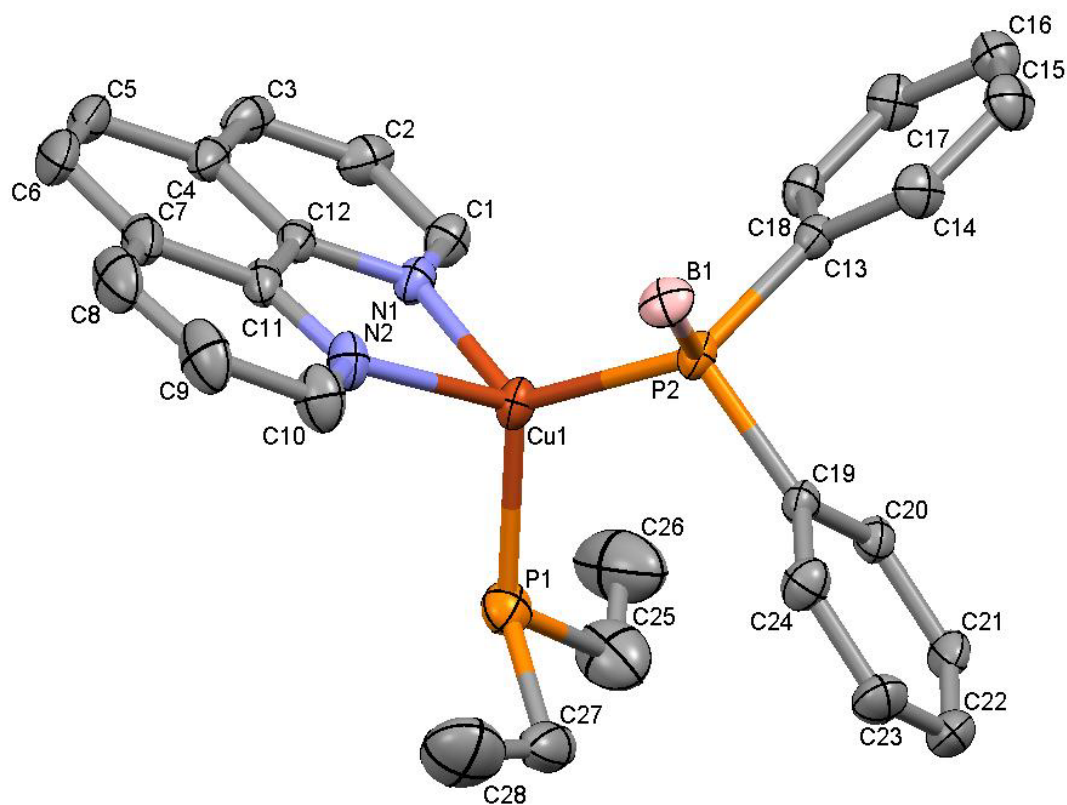
(IV) Synthesis of alkynylphosphine **6** using a catalytic amount of complex **4a** or **4b**

In a Schlenk tube, flushed with nitrogen, were introduced complex **4a** (16 mg, 0.025 mmol, 10 mol%) or **4b** (13 mg, 0.025 mmol, 10 mol%), phosphine-borane **1** (50 mg, 0.25 mmol, 1 equiv.), and K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.). After cooling to −60 °C, degassed dry toluene (3 mL) and a solution of 1-bromohexyne (**5**) (48 mg, 0.30 mmol, 1.2 equiv.) in degassed dry toluene (1 mL) were successively added. After stirring for 30 min, the cool bath was removed and the reaction mixture was stirred at rt overnight. Next the reaction mixture was filtered over celite with toluene as the eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with pentane/toluene (6:4) as the eluent. The alkynylphosphine **6** was obtained in 80% (56 mg) and 81% (57 mg) yields using complexes **4a** and **4b** respectively.

(V) NMR spectra
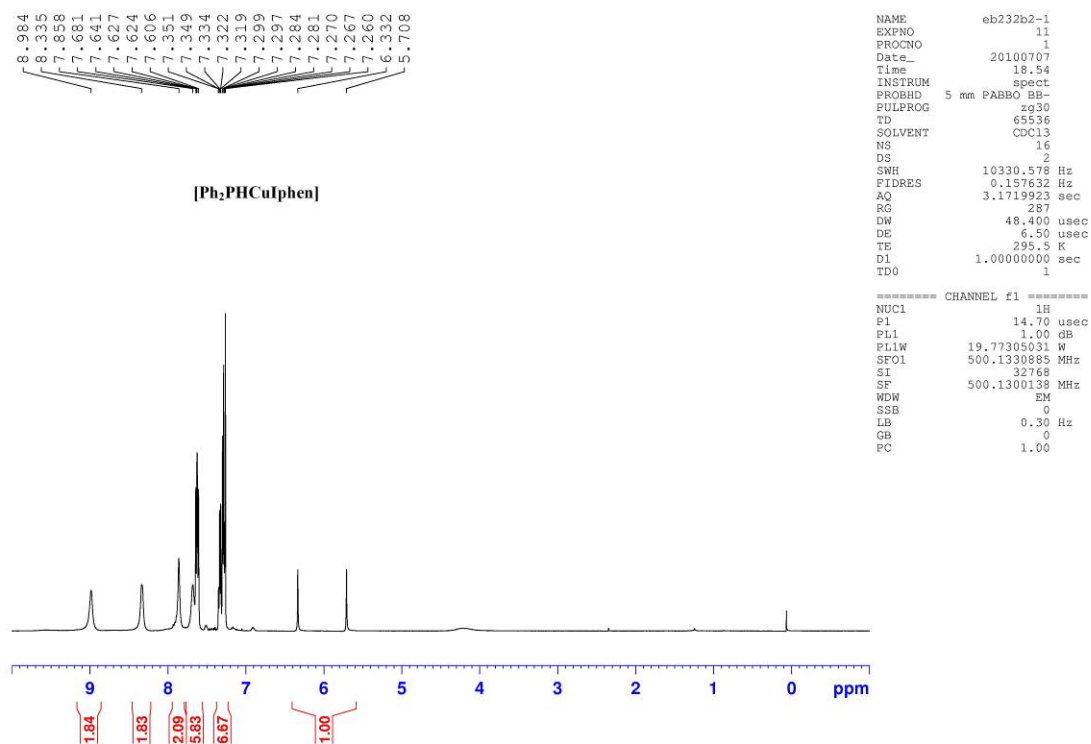
[Ph₂PHCuIphen]

^{1}H NMR (500 MHz, CDCl$_3$) spectrum of complex [Ph$_2$PHCuIphen] **(3a)**

[Ph₂PHCuIphen]

^{13}C NMR (125 MHz, CDCl$_3$) spectrum of complex [Ph$_2$PHCuIphen] **(3a)**

−32.23

[Ph$_2$PHCuIphen]

NAME   eb232b2-1
EXPNO   14
PROCNO   1
Date_   20100707
Time   19.54
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zgpg30
TD   65536
SOLVENT   CDCl3
NS   64
DS   4
SWH   81521.742 Hz
FIDRES   1.243923 Hz
AQ   0.4020041 sec
RG   2050
DW   6.133 usec
DE   6.50 usec
TE   295.3 K
D1   2.00000000 sec
D11   0.03000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   31P
P1   11.00 usec
PL1   4.80 dB
PL1W   28.52949524 W
SFO1   202.4462121 MHz

======== CHANNEL f2 ========
CPDPRG2   waltz16
NUC2   1H
PCPD2   80.00 usec
PL2   1.00 dB
PL12   15.72 dB
PL13   15.72 dB
PL2W   19.77305031 W
PL12W   0.66691983 W
PL13W   0.66691983 W
SFO2   500.1325007 MHz
SI   131072
SF   202.4563350 MHz
WDW   EM
SSB   0
LB   25.00 Hz
GB   0
PC   0.50

^{31}P NMR (202 MHz, CDCl$_3$) spectrum of complex [Ph$_2$PHCuIphen] **(3a)**

NAME   aib CuI Et2P
EXPNO   11
PROCNO   1
Date_   20110408
Time   0.04
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zg30
TD   65536
SOLVENT   CD2Cl2
NS   16
DS   2
SWH   10330.578 Hz
FIDRES   0.157632 Hz
AQ   3.1719923 sec
RG   161
DW   48.400 usec
DE   6.50 usec
TE   297.2 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   14.70 usec
PL1   1.00 dB
PL1W   19.77305031 W
SFO1   500.1330885 MHz
SI   32768
SF   500.1300205 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00

^{1}H NMR (500 MHz, CD$_2$Cl$_2$) spectrum of complex [Et$_2$PHCuIphen] **(3b)**

149.822
143.665
136.689
129.464
127.054
124.895
54.273
54.056
53.840
53.623
53.407
14.487
14.329
11.433
11.419

NAME   aib CuI Et2P
EXPNO   23
PROCNO   1
Date_   20110408
Time   4.51
INSTRUM   spect
PROBHD   5 mm TXO 31P/1
PULPROG   zgpg30
TD   65536
SOLVENT   CD2Cl2
NS   2048
DS   2
SWH   31250.000 Hz
FIDRES   0.476837 Hz
AQ   1.0486259 sec
RG   2050
DW   16.000 usec
DE   8.00 usec
TE   298.0 K
D1   1.00000000 sec
D11   0.03000000 sec
TD0   1

-------- CHANNEL f1 --------
NUC1   13C
P1   8.00 usec
PL1   0.00 dB
PL1W   90.85493469 W
SFO1   125.7703648 MHz

-------- CHANNEL f2 --------
CPDPRG2   waltz16
NUC2   1H
PCPD2   80.00 usec
PL2   -1.00 dB
PL12   18.00 dB
PL13   18.00 dB
PL2W   31.33817101 W
PL12W   0.39452422 W
PL13W   0.39452422 W
SFO2   500.1316005 MHz
SI   131072
SF   125.7577466 MHz
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of complex [Et_2PHCuIphen] **(3b)**

-40.91

NAME   aib CuI Et2P
EXPNO   10
PROCNO   1
Date_   20110407
Time   23.59
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zgpg30
TD   65536
SOLVENT   CD2Cl2
NS   64
DS   4
SWH   81521.742 Hz
FIDRES   1.243923 Hz
AQ   0.4020041 sec
RG   2050
DW   6.133 use
DE   6.50 use
TE   297.7 K
D1   2.00000000 sec
D11   0.03000000 sec
TD0   1

======== CHANNEL f1 =======
NUC1   31P
P1   11.00 use
PL1   4.80 dB
PL1W   28.52949524 W
SFO1   202.4462121 MHz

======== CHANNEL f2 =======
CPDPRG2   waltz16
NUC2   1H
PCPD2   80.00 use
PL2   1.00 dB
PL12   15.72 dB
PL13   15.72 dB
PL2W   19.77305031 W
PL12W   0.66691983 W
PL13W   0.66691983 W
SFO2   500.1325007 MHz
SI   131072
SF   202.4563350 MHz
WDW   EM
SSB   0
LB   15.00 Hz
GB   0
PC   1.40

^{31}P NMR (202 MHz, CD_2Cl_2) spectrum of complex [Et_2PHCuIphen] **(3b)**

^{1}H NMR (500 MHz, CD$_2$Cl$_2$) spectrum of complex [Ph$_2$PHCuPPh$_2$BH$_3$phen] (**4a**)

^{13}C NMR (125 MHz, CD$_2$Cl$_2$) spectrum of complex [Ph$_2$PHCuPPh$_2$BH$_3$phen] (**4a**)

—20.57

—31.84
—33.35

NAME   aib 104 apres puri
EXPNO   12
PROCNO   1
Date_   20110622
Time   0.45
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zg30
TD   65536
SOLVENT   CD2Cl2
NS   64
DS   4
SWH   81521.742 Hz
FIDRES   1.243923 Hz
AQ   0.4020041 sec
RG   2050
DW   6.133 use
DE   6.50 use
TE   295.0 K
D1   2.00000000 sec
TD0   1

======== CHANNEL f1 =======
NUC1   31P
P1   11.00 use
PL1   4.80 dB
PL1W   28.52949524 W
SFO1   202.4563350 MHz
SI   131072
SF   202.4563350 MHz
WDW   EM
SSB   0
LB   10.00 Hz
GB   0
PC   1.40

30   20   10   0   −10   −20   −30   −40   −50   −60   ppm

^{31}P NMR (202 MHz, CD$_2$Cl$_2$) spectrum of complex [Ph$_2$PHCuPPh$_2$BH$_3$phen] (**4a**)

—32
—32

PROCNO   1
Date_   20110622
Time   0.49
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zgpg30
TD   65536
SOLVENT   CD2Cl2
NS   64
DS   4
SWH   32051.281 Hz
FIDRES   0.489064 Hz
AQ   1.0224116 sec
RG   362
DW   15.600 usec
DE   6.50 usec
TE   295.2 K
D1   1.00000000 sec
D11   0.03000000 sec
TD0   1

======== CHANNEL f1 ====
NUC1   11B
P1   7.50 usec
PL1   0.00 dB
PL1W   86.66007996 W
SFO1   160.4615792 MHz

======== CHANNEL f2 ====
CPDPRG2   waltz16
NUC2   1H
PCPD2   80.00 usec
PL2   1.00 dB
PL12   15.72 dB
PL13   15.72 dB
PL2W   19.77305031 W
PL12W   0.66691983 W
PL13W   0.66691983 W
SFO2   500.1316005 MHz
SI   32768
SF   160.4615790 MHz
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm

^{11}B NMR (160 MHz, CD$_2$Cl$_2$) spectrum of complex [Ph$_2$PHCuPPh$_2$BH$_3$phen] (**4a**)

^{1}H NMR (500 MHz, CD$_2$Cl$_2$) spectrum of complex [Et$_2$PHCuPPh$_2$BH$_3$phen] (**4b**)

^{13}C NMR (125 MHz, CD$_2$Cl$_2$) spectrum of complex [Et$_2$PHCuPPh$_2$BH$_3$phen] (**4b**)

NAME   aib 066 Et2PhCuPPh2BH
EXPNO   11
PROCNO   1
Date_   20110428
Time   23.47
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zg30
TD   65536
SOLVENT   CD2Cl2
NS   64
DS   4
SWH   81521.742 Hz
FIDRES   1.243923 Hz
AQ   0.4020041 sec
RG   2050
DW   6.133 usec
DE   6.50 usec
TE   297.5 K
D1   2.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   31P
P1   11.00 usec
PL1   4.80 dB
PL1W   28.52949524 W
SFO1   202.4563350 MHz
SI   131072
SF   202.4563350 MHz
WDW   EM
SSB   0
LB   5.00 Hz
GB   0
PC   1.40

^{31}P NMR (202 MHz, CD$_2$Cl$_2$) spectrum of complex [Et$_2$PHCuPPh$_2$BH$_3$phen] (**4b**)

Date_   20110620
Time   22.23
INSTRUM   spect
PROBHD   5 mm PABBO
PULPROG   zgpg30
TD   65536
SOLVENT   CD2Cl2
NS   64
DS   4
SWH   32051.281 H
FIDRES   0.489064 H
AQ   1.0224116 se
RG   362
DW   15.600 use
DE   6.50 usec
TE   295.4 K
D1   1.00000000 se
D11   0.03000000 se
TD0   1

======== CHANNEL f1
NUC1   11B
P1   7.50 usec
PL1   0.00 dB
PL1W   86.66007996
SFO1   160.4615792

======== CHANNEL f2
CPDPRG2   waltz16
NUC2   1H
PCPD2   80.00 us
PL2   1.00 dB
PL12   15.72 dB
PL13   15.72 dB
PL2W   19.77305031
PL12W   0.66691983
PL13W   0.66691983
SFO2   500.1316005
SI   32768
SF   160.4615790 M
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

^{11}B NMR (160 MHz, CD$_2$Cl$_2$) spectrum of complex [Et$_2$PHCuPPh$_2$BH$_3$phen] (**4b**)

(VI) Theoretical studies

The nature of the copper phosphido-borane bond in complexes **4** was investigated using electron localization function (ELF)[i] and atoms in molecules (AIM) theoretical studies.[ii] ELF topological analysis is a unique tool for chemical bonding studies, as it provides a partition of the molecular space into basins that are in one-to-one correspondence with classical Lewis-type electronic units such as cores, bonds and lone pairs.[1b] The populations and (co)variances of these valence basins can be further interpreted in terms of weighted combinations of mesomeric structures.[iii]

ELF and AIM analyses of copper complexes **4a** and **4b** were performed at the B3PW91/DGDZVP level using the experimental geometries. AIM atomic charges and average populations of selected ELF valence basins are given in Figure S1.
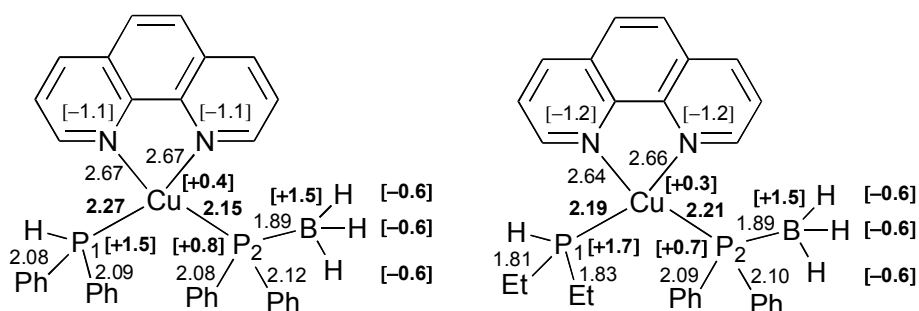
Figure S1. Average populations of selected ELF valence basins of complex **4a** (left) and **4b** (right). Atomic AIM charges in brackets. Calculation performed at the B3PW91/DGDZVP level, on the experimental geometry.

The ELF picture of various phosphorus ligands is summarized in Table S1.

Ligand	PPh_3	$HPPh_2$	H_3BPPh_2	$(PPh_2)^-$
$V(P)$	2.13	2.14	2.12	2 x 1.94
$V(P, C_{ipso})$	2.11	2.04	2.12	2.15
	2.11	2.08	2.08	
	2.12			
Q_{AIM} (P)	+ 1.5	+ 1.5	+ 0.6	+ 0.6
f_{ELF} (V(P))	0.35	0.32	0.40	2 x 0.27
f_{AIM} (P)	0.40	0.37	0.55	0.57

Table S1. Atomic AIM charge of P (Q_{AIM} (P)) and average population of selected ELF valence basins in various phosphines and phosphide ligands. B3PW91/6-31G**//PCM-B3PW91/6-31G** level of calculation.

The results of the frontier molecular orbital analysis of various phosphorus ligands are given on Figure S2.

Energy (au)
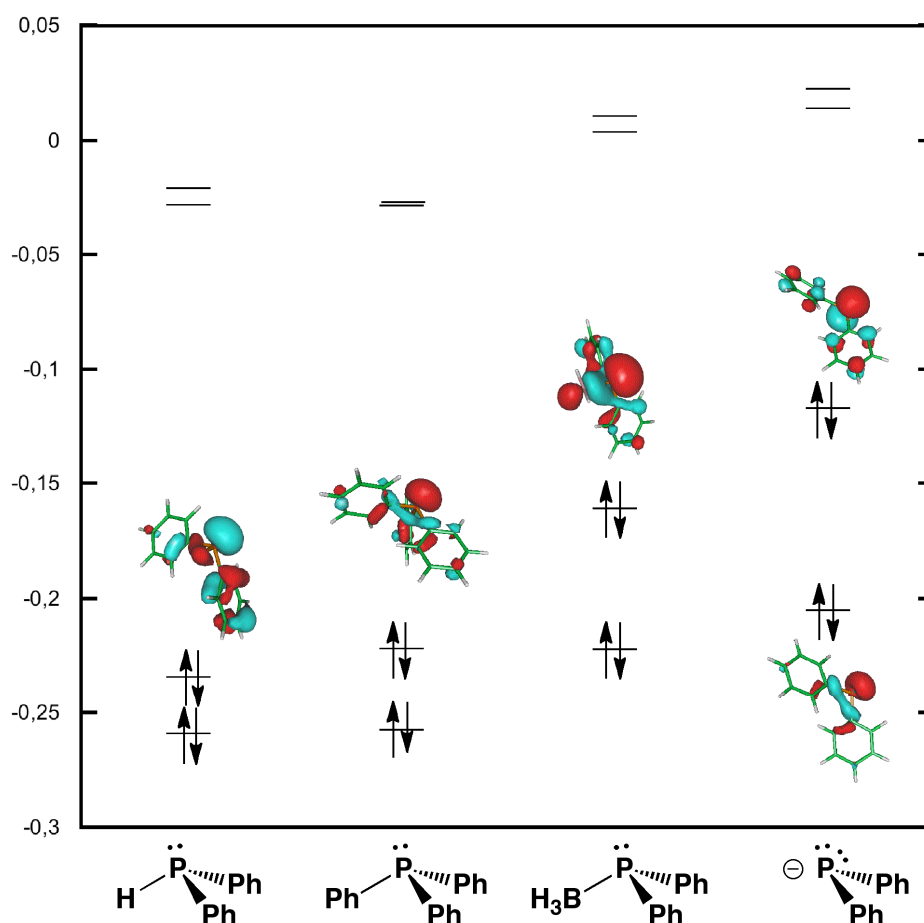
Figure S2. Comparison of near-frontier molecular orbitals of various phosphorus ligands. PCM-B3PW91/6-31G** calculation in dichloromethane.

The molecular orbitals corresponding to the σ bonds in complex **4a** are given in Figure S3.
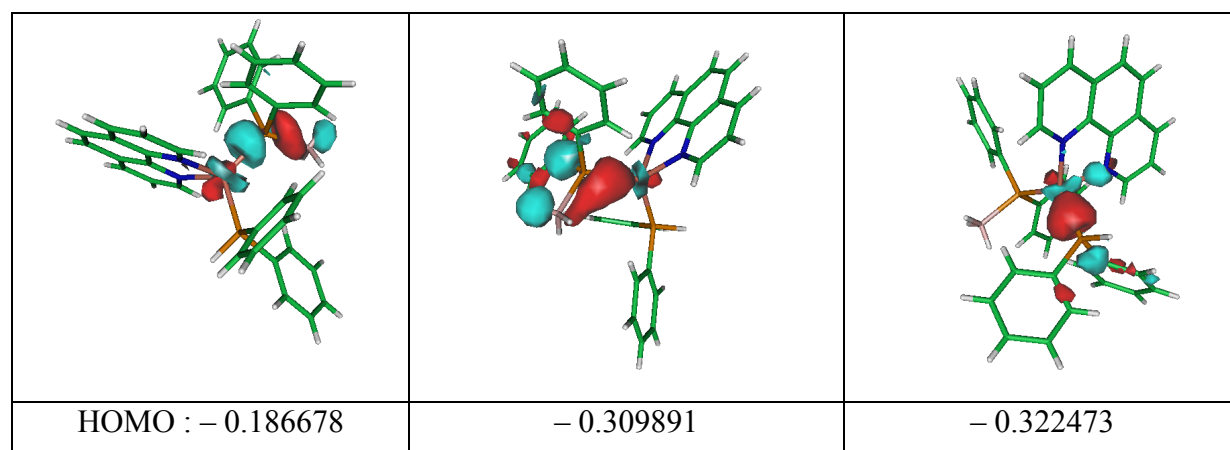

| HOMO : − 0.186678 | − 0.309891 | − 0.322473 |

Figure S3. Molecular orbitals of complex **4a** related to the Cu-P σ-bonds. PCM-B3PW91/6-31G** calculation in dichloromethane.

Bond dissociation energies of phosphine and phosphido-borane ligands in complex **4a** are compared in Table S2

Dissociated ligand	$HPPh_2$	$H_3B\text{-}PPh_2$
$\Delta E_{diss}{}^{a}$	14.48	31.88
$\Delta E_{diss} + ZPE$	13.13	30.57
$\Delta G_{diss}{}^{a}$	−1.52	16.21

Table S2. Heterolytic dissociation energies (in kcal/mol) calculated at the PCM-B3PW91/6-31G** level in dichloromethane using relaxed fragments as references. $^{a}\Delta E$ refers to the dissociation energy calculated at 0 K whereas ΔG refers to the Gibbs dissociation energy calculated at 298.15K.

The above theoretical studies suggest that the phosphido-borane ligand is of L type in the Green formalism.[iv] The 18e copper complex **4a** may be described by the mesomeric form of Figure S4.
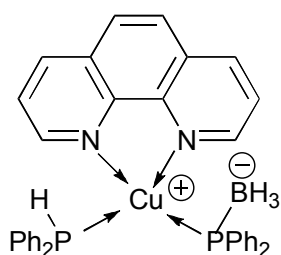
Figure S4. Mesomeric form describing the chemical bonding in copper complex **4a**.

The relative chemical reactivity of the Cu-P$_1$ and Cu-P$_2$ bonds was further investigated using Fukui indices. The Fukui fonction was introduced by Parr and Yang as the response of the electron density of the molecular system to a change in the global number of electrons.[v] It can be expressed as the derivative of the electron density $\rho(r)$ with respect to the number of electrons N, calculated at a constant external potential v(r). Because of the discontinuity in this derivative, left and right derivatives have to be considered. The local Fukui functions $f^{+}(r) = (\partial\rho/\partial N)^{+}{}_{v}$ and $f^{-}(r) = (\partial\rho/\partial N)^{-}{}_{v}$ are therefore the response for adding or removing electron from the system and allow for investigation of nucleophilic and electrophilic attack respectively.

The finite difference approach ($\Delta N = \pm\ 1$) allows for estimation of approximate local Fukui functions $f(r)$ from the electron density $\rho(r)$ or of atomic Fukui indices $f(A)$ from atomic charges Q(A):[vi]

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \; ; f^-(r) = \rho_N(r) - \rho_{N-1}(r)$$

$$f^+(A) = Q_N(A) - Q_{N+1}(A) \; ; f^-(A) = Q_{N-1}(A) - Q_N(A)$$

Recently, alternative schemes relying on the condensation of frontier molecular orbital (FMO) Fukui functions within an AIM[vii] or ELF[viii] topological partition have been disclosed:

$$f_X^{\alpha}(r) = \int_X |\phi_{KS}^F(r)|^2 \, dr$$

is the contribution of the FMO F ($\alpha = -$: F = HOMO ; $\alpha = +$: F = LUMO) to the atomic AIM basin or to the core or valence ELF basin X. The latter indices are more attractive than the above atomic indices because they are confined in the 0 to 1 range and they sum up to one: $0 \le f_X^{\alpha} \le 1$ et $\sum_X f_X^{\alpha} = 1$. The larger the value of the f index, the more reactive the corresponding basin X.

The dual reactivity descriptor $\Delta f = f^+(r) - f^-(r)$ may also be used for the simultaneous detection of the nucleophilic or electrophilic behavior of a given site and is especially useful for ambiphilic reagents.[ix]

The sensitivity of copper complex **4a** towards the electrophilic attack such as the one of an alkynyl halide was investigated using Fukui functions f^- condensed on ELF or AIM basins. Their values calculated at the B3PW91/DGDZVP level using the experimental geometry of **4a** are given on Figure S5.
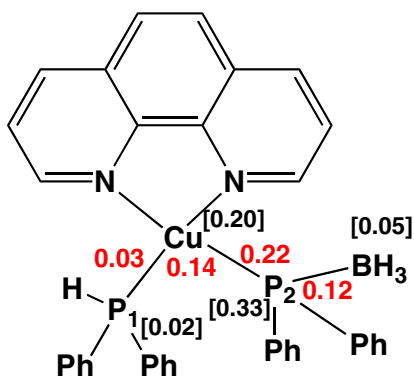

Figure S5. Selected Fukui functions f^- condensed on ELF (in red) or AIM (in brackets) basins of copper complex **4a**. B3PW91/DGDZVP calculation performed on the experimental geometry.

The ^{31}P and ^{11}B NMR spectra of complex **4a** were calculated at the GIAO/B3PW91/6-31+G** level. The calculated chemical shifts and spin coupling constants are in good agreement with the experimental data (Table S3).

	δ_P (ppm)	δ_B (ppm)	$^2J_{PP}$ (Hz)	$^1J_{PB}$ (Hz)
Exp.	−32.56 (P$_1$)	−32.40		
	−20.53 (P$_2$)			
Calcd	−33.57 (P$_1$)	−37.96	74.70	−0.15 (P$_1$)
	−22.74 (P$_2$)			55.17 (P$_2$)

Table S3. Comparaison of experimental and calculated ^{31}P and ^{11}B NMR spectra of complex **4a**. B3PW91/6-31+G**//B3PW91/6-31G**/LANL2DZ(Cu) level of calculation.

Computational details

Geometries were fully optimized at the PCM-B3PW91/6-31G**/LANL2DZ*(Cu) level of calculation using Gaussian09.[x] LANL2DZ*(Cu) means that f-polarization functions derived by Ehlers et al.[xi] for Cu have been added to the LANL2DZ(Cu) basis set. Vibrational analysis was performed at the same level as the geometry optimization. Solvent effects were included using the polarizable continuum model (PCM) implemented in Gaussian09 (dichloromethane solvent, $\varepsilon=8.93$).

The magnetic shielding tensor and nuclear spin coupling constants were calculated at the B3PW91/6-31+G** level using the GIAO (gauge-independent atomic orbital) method implemented in Gaussian09.[10] The ^{31}P NMR chemical shifts were estimated with respect to the usual H_3PO_4 reference and the ^{11}B NMR chemical shifts were estimated with respect to the usual $BF_3{\cdot}OEt_2$ reference.

Atoms in molecules (AIM) and electron localization function (ELF) analyses were performed with the TopMoD package.[xii]

Molecular orbitals were plotted using the GABEDIT program.[xiii]

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