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Biphosphinine-copper(I) complexes: chelate vs polymeric helical structures[†]

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Summary — Upon reaction with $[Cu(MeCN)_4]^+$, 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) gives a $[Cu(tmbp)(MeCN)_2]^+$ cationic chelate which is a convenient source for a variety of $[Cu(tmbp)L_2]^+$ complexes with L = Et_2S, Ph_3As, Ph_3P, dppe and pyridine. The X-ray crystal structure analysis of the complex with L = Ph_3P shows a chelate structure weakened by the non-coplanarity of the two phosphinine rings and by the absence of electronic delocalization. In fact, the tmbp ligand can indifferently adopt a chelating or a bis (η^1-P) complexing mode toward the copper(I) center as shown by the reaction of a 1:1 mixture of 2,2′-bipyridine (bpy) and tmbp with $[Cu(MeCN)_4]^+$. A polymeric helix is thus produced where [Cu(bpy)] subunits are bridged by tmbp acting as two separate P-donors.

2,2′-biphosphinine / 2,2′-bipyridine / copper(I) complex / helical structure

Résumé — Complexes de biphosphinine cuivre(I) présentant une structure chélate ou en hélice. *La réaction de la 4,4′,5,5′-tétraméthyl-2,2′-biphosphinine (tmbp) avec $[Cu(MeCN)_4]^+$ fournit un chelate cationique $[Cu(tmbp)(MeCN)_2]^+$ qui est un bon précurseur de complexes du type $[Cu(tmbp)L_2]^+$ avec L = Et_2S, Ph_3As, Ph_3P, dppe, pyridine. L'analyse aux rayons X de la structure du complexe avec L = PPh_3 montre une structure chélate affaiblie par la non-coplaneité des deux noyaux phosphinine et par l'absence de délocalisation électronique. Il apparaît que la biphosphinine peut adopter indifféremment deux modes de coordination avec le cuivre(I), soit le mode chélatant, soit le mode pontant bis (η^1-P). Ainsi, la réaction d'un mélange 1:1 de 2,2′-bipyridine (bpy) et de biphosphinine (tmbp) avec le cation $[Cu(MeCN)_4]^+$ fournit un polymère en hélice dans lequel les unités chélatées [Cu(bpy)] sont pontées par des biphosphinines se comportant comme deux donneurs phosphorés indépendants.*

2,2′-biphosphinine / 2′,2′-bipyridine / complexe de cuivre(I) / structure en hélice

Introduction

Since our discovery of 2,2′-biphosphinines [1], we have undertaken a systematic investigation of their coordination behavior [2] in order to delineate analogies and differences with the extensive coordination chemistry of their nitrogen counterparts, the ubiquitous 2,2′-bipyridines. In this paper, we report the results obtained with copper(I) centers. Several reasons underlie our choice. Firstly, copper-biphosphine chelates have shown some promise as anticancer drugs [3]. Secondly, 2,2′-bipyridines form the backbone of several ligands which are used to create double and triple helicate structures [4]. One of the first of such structures described is based on 2,2′-bipyridine-copper(I) subunits [5]. Finally, the 2,2′-bipyridine-copper(I) chelates display some interesting spectroscopic, luminescence and electrochemical properties [6].

Results and discussion

The reaction of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) **1** with the $[Cu(MeCN)_4][BF_4]$ cationic complex, in a 1:1 ratio at room temperature directly affords the monochelate **2** in high yield (eq 1).

This chelate is an ideal precursor for the synthesis of a variety of other cationic complexes via the displacement of the two acetonitrile molecules by other $2e^-$ donor ligands as shown in eq 2.

The triphenylphosphine complex **5** displays an A_2X_2 ^{31}P NMR spectrum in good agreement with the expected tetrahedral geometry. In fact, the X-ray crystal structure analysis of **5** (fig 1) shows a significantly distorted structure with a $P_1CuP_{1'}/P_9CuP_{9'}$ angle of 74.35 ± 0.03°. The chelation induces a strong deviation of the bond angles at copper. The small bite P_1-Cu-$P_{1'}$ [83.22(5)°] and the large PPh_3-Cu-PPh_3 angle [129.49(5)°] are comparable with the correspond-

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[†] Dedicated to Prof Raymond Weiss.

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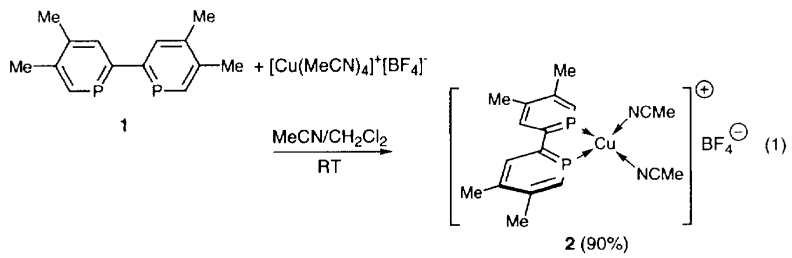
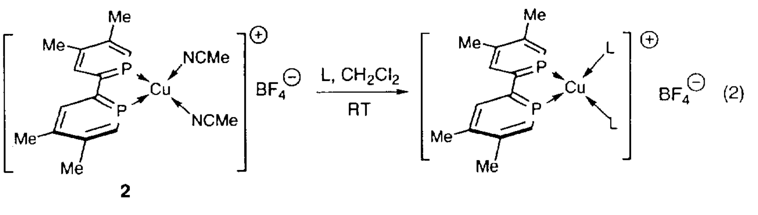




3 L = Et_2S (95%)
4 L = Ph_3As (90%)
5 L = Ph_3P (95%)
6 $L_2 = [Ph_2PCH_2]_2$ (95%)
7 L = C_5H_5N (85%)

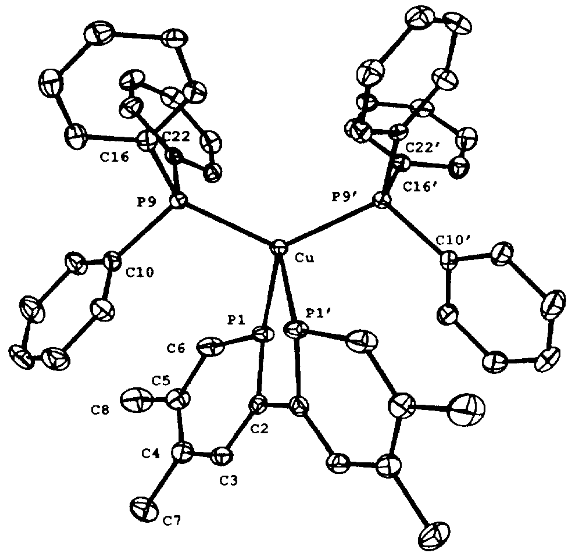


Fig 1. Ortep drawing of one molecule of **5**, as determined by a single crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu-P(1) 2.3273(9), Cu-P(1') 2.3286(9), Cu-P(9) 2.2841(8), Cu-P(9') 2.2843(8), P(1)-C(2) 1.733(3), P(1)-C(6) 1.721(4), C(2)-C(2') 1.490(6), C(2)-C(3) 1.389(4), C(3)-C(4) 1.392(5), C(4)-C(5) 1.405(5), C(5)-C(6) 1.382(5); P(1)-Cu-P(1') 83.22(5), P(1)-Cu-P(9) 99.02(3), P(1)-Cu-P(9') 118.76(3), P(9)-Cu-P(9') 129.49(5), Cu-P(1)-C(2) 108.5(1), C(2)-P(1)-C(6) 101.9(2), P(1)-C(2)-C(2') 113.9(1).

ing angles found in $[Cu(bpy)(PPh_3)_2]^+$, respectively, 79.6(4) and 125.4(1)° [8]. The less expected features concern the non-coplanarity of the two phosphinine rings (inter-ring angle of 39.85 ± 0.12°) and the rather long P_1-Cu and $P_{1'}$-Cu bond distances (2.3273(9) and 2.3286(9) Å respectively). These two values can be compared with those recorded for the only known example of a phosphinine-copper(I) complex (2.223(3) Å) [9]. The origin of the non-coplanarity of the two phosphinine rings can be found in the necessity to partly alleviate the strain within the chelate ring by expanding the P_1-Cu-$P_{1'}$ angle. Another unexpected feature concerns the π,π interaction between each phosphinine ring and one phenyl ring of each triphenylphosphine, see figure 2. As a result of the distortion of the biphosphinine, the copper atom lies outside of the two phosphinine planes by 1.216 (P_1-C_6) and −1.217 Å ($P_{1'}$-$C_{6'}$). Consequently, the overlap between the lone pair orbitals of the phosphinines and the copper *d* orbitals is reduced and the P_1-Cu and $P_{1'}$-Cu bonds are weakened. That the interaction between the copper cen-

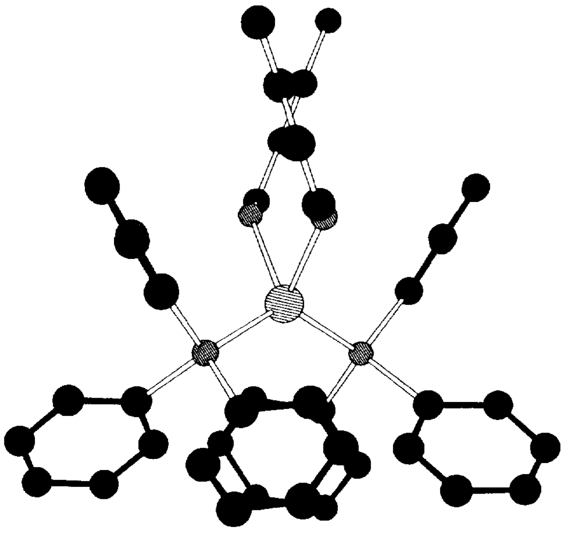
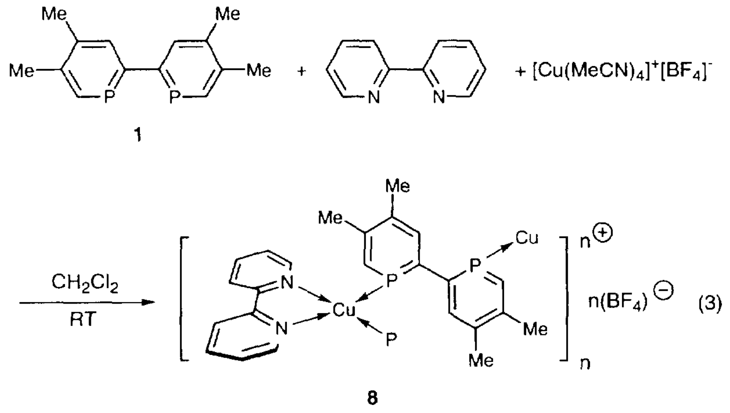


Fig 2. The interaction between phosphinine rings and one phenyl ring of each triphenylphosphine in $[Cu(tmbp)(PPh_3)_2][BF_4]$ **5**.



ter and the biphosphinine is relatively weak can also be detected in the structural parameters of the chelating ligand. These parameters are closely similar to those of the free ligand in its cisoid geometry [10]. In particular, the C_2-$C_{2'}$ bridge has exactly the same length in both cases, 1.490 Å. Thus, no electronic delocalization occurs within the five-membered C_2P_2Cu chelate ring and hence no strengthening of the complex, contrary to what is observed in $[W(tmbp)_3]$ for example [2].

The relative lability of the biphosphinine-copper(I) chelates is also spectacularly illustrated by the results obtained during the study of mixed biphosphinine-bipyridine-copper(I) complexes. Upon mixing (tmbp), (bpy) and $[Cu(MeCN)_4][BF_4]$ in a 1:1:1 ratio, a yellow, poorly soluble, precipitate of **8** is formed (eq 3).

The same complex is also obtained by reaction of tmbp with $[Cu(bpy)_2][BF_4]$ at room temperature in CH_2Cl_2. It has been characterized by ^{31}P and ^{1}H NMR and microanalysis. Its structure has been established by X-ray analysis (figs 3 and 4). Complex **8** displays an helix polymeric structure where [Cu(bpy)] planar subunits are connected together by the biphosphinine acting as two independent P-donors. A close inspection of this structure leads to several interesting observations. Firstly, the [Cu(tmbp)] is apparently less stable than the [Cu(bpy)] chelate unit, thus confirming our analysis above. Secondly, the [Cu(bpy)] units in **8** display a geometry which is closely similar to that observed in $[Cu(bpy)(PPh_3)_2]^+$ [8]. The biphosphinine-copper(I) links are apparently stronger in **8** than in **5**, 2.2542(6) and 2.2090(6) Å vs 2.3273(9) and 2.3286(9) Å, and are close to those observed in a monophosphinine-copper(I) complex [9]. In fact, the copper lies closer to the phosphinine plane in **8** than in **5**: the distance to the plane is only 0.713 Å in **8**, thus allowing a better overlap between the phosphinine lone pair and the copper *d* orbitals. Finally, the geometry of the biphosphinine in **8** is transoid (interplane angle 129.85 ± 0.09°) and the C_6-C_7 bridge at 1.481(3) Å has the same length as in the transoid form of the free ligand, 1.484(6) Å [10].

The fact that biphosphinine can switch easily from a chelating to a bis-η^1-complexing mode with copper(I) has several chemical implications that we are currently exploring.

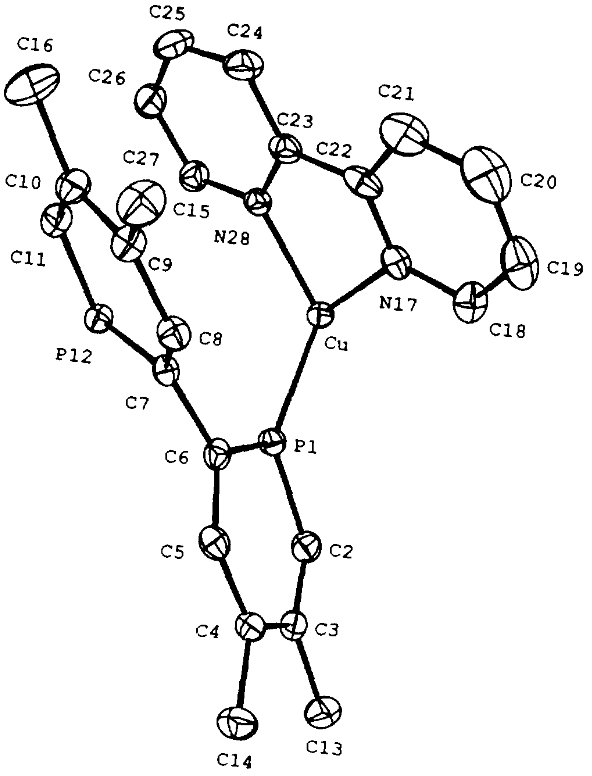


Fig 3. Ortep drawing of one subunit of **8**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu-P(1) 2.2542(6), Cu-P(12) 2.2090(6), Cu-N(17) 2.075(2), Cu-N(28) 2.040(2), P(1)-C(6) 1.721(2), P(1)-C(2) 1.714(2), C(6)-C(7) 1.481(3); P(1)-Cu-P(12) 109.34(2), N(17)-Cu-N(28) 79.53(8), C(2)-P(1)-C(6) 103.2(1).

Experimental section

Reactions were performed under nitrogen using oven-dried glassware. Dry ether, toluene and hexane were obtained by double distillation from Na/benzophenone, dry CH_2Cl_2 was obtained from P_2O_5 and dry acetonitrile from distillation over CaH_2. Celite, for filtration, was dried under vacuum at 120 °C. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at

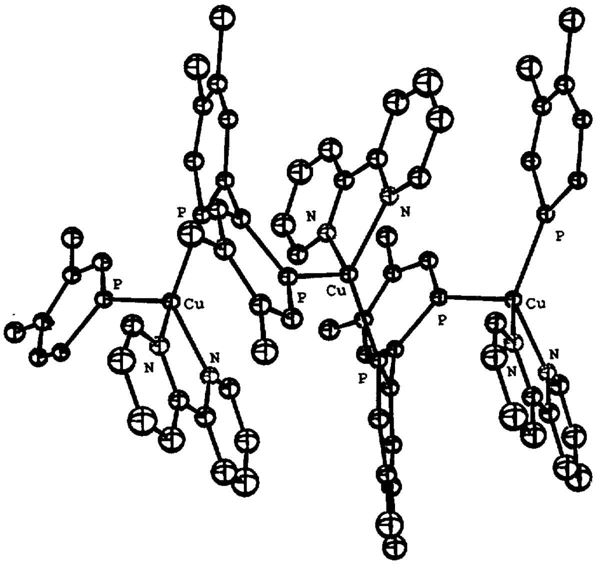


Fig 4. Ortep representation of three subunits of the polymeric chain of **8**.

200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad, p = pseudo), integration, and coupling constants in hertz. Elemental analyses were performed by the Service d'analyse du CNRS, at Gif-sur-Yvette, France. Starting materials were obtained from commercial suppliers or prepared according to literature methods ([Cu(MeCN)$_4$][BF$_4$]) [11].

[Cu(tmbp)(MeCN)$_2$][BF$_4$] 2

Biphosphinine **1** (2.46 g, 10 mmol) was added at room temperature to a solution of [Cu(MeCN)$_4$][BF$_4$] (3.14 g, 10 mmol) in MeCN (20 mL) and CH_2Cl_2 (20 mL). After 10 min of stirring, the solvents were evaporated yielding a yellow solid which was washed with hexane (3 x 10 mL). CH_2Cl_2 (50 mL) was then added and the resulting solution was filtered. After evaporation of the solvent, complex **2** was recovered as a yellow solid which was crystallized in a CH_2Cl_2/hexane (2:1) mixture. Yield: 4.30 g (90%).

^{31}P NMR (CD_2Cl_2): δ 149.40.

^1H NMR (CD_2Cl_2): δ 2.10 (s, 6H, Me of MeCN), 2.37 (s, 6H, Me of tmbp), 2.43 (s, 6H, Me of tmbp), 7.92 (pt, AXX', 2H, ΣJ (H-P) = 28.51, $H_{6,6'}$), 8.01 (pt, AXX', 2H, ΣJ (H-P) = 11.40, $H_{3,3'}$).

^{13}C NMR (CD_2Cl_2): δ 2.95 (s, Me of MeCN), 23.55 (s, Me of tmbp), 23.90 (s, Me of tmbp), 119.25 (s, -C≡N), 136.90 (bs, $C_{3,3'}$ of tmbp), 143.85 (pt, AXX', ΣJ (C-P) = 24.40, $C_{4,4'}$ or $C_{5,5'}$), 145.90 (bs, $C_{6,6'}$), 148.50 (pt, AXX', ΣJ (C-P) = 13.75, $C_{4,4'}$ or $C_{5,5'}$), 160.17 (pt, AXX', ΣJ (C-P) = 27.50, $C_{2,2'}$).

Anal calc for $C_{18}H_{22}BCuF_4N_2P_2$: C, 45.17; H, 4.63. Found: C, 45.78; H, 4.75.

[Cu(tmbp)(Et$_2$S)$_2$][BF$_4$] 3

Diethyl sulfide (0.9 g, 10 mmol) was added to a solution of complex **2** (0.48 g, 1 mmol) in CH_2Cl_2 (10 mL). After 10 min of stirring, the solution was filtered and the solvent and the excess of diethyl sulfide were evaporated yielding a yellow oil. Yield: 0.55 g (95%).

^{31}P NMR ($CDCl_3$): δ 139.25.

^1H NMR ($CDCl_3$): δ 1.25 (t, 12H, ^3J (H-H) = 7.40, Me of Et), 2.52 (m, 12H, Me of tmbp), 2.67 (q, 8H, ^3J (H-H) = 7.40, CH_2 of Et), 8.22–8.38 (m, 4H, $H_{3,3'}$ and $H_{6,6'}$).

^{13}C NMR ($CDCl_3$): δ 14.50 (s, Me of Et), 23.80 (s, Me of tmbp), 24.35 (s, Me of tmbp), 29.45 (s, CH_2 of Et), 134.51 (bs, $C_{3,3'}$ of tmbp), 143.30 (pt, AXX', ΣJ (C-P) = 22.25, $C_{4,4'}$ or $C_{5,5'}$), 146.80 (bs, $C_{6,6'}$), 148.15 (pt, AXX', ΣJ (C-P) = 13.50, $C_{4,4'}$ or $C_{5,5'}$), 160.65 (pt, AXX', ΣJ (C-P) = 29.0, $C_{2,2'}$).

Anal calc for $C_{22}H_{36}BCuF_4P_2S_2$: C, 45.80; H, 6.29. Found: C, 45.55; H, 6.38.

[Cu(tmbp)(AsPh$_3$)$_2$][BF$_4$] 4

Triphenylarsine (0.67 g, 2.2 mmol) was added to a solution of complex **2** (0.48 g, 1 mmol) in CH_2Cl_2 (20 mL). As the arsine was added, the complex started to precipitate. After 10 min of stirring, the CH_2Cl_2 was evaporated and 20 mL hexane was added. A filtration of the hexane phase allows the elimination of the excess arsine. The resulting solid was then dissolved in CH_2Cl_2 (50 mL) and the resulting solution was filtered. After evaporation and drying, complex **4** was recovered as a bright yellow solid. Yield: 0.9 g (90%).

^{31}P NMR (CD_2Cl_2): δ 152.15.

^1H NMR (CD_2Cl_2): δ 2.31 (s, 6H, Me of tmbp), 2.45 (s, 6H, Me of tmbp), 7.01–7.35 (m, 30H, CH of C_6H_5), 7.85 (pt, 2H, AA'XX', ΣJ (H-P) = 31.10, $H_{6,6'}$), 8.31 (m, AA'XX', 2H, $H_{3,3'}$).

Anal calc for $C_{50}H_{46}As_2BCuF_4P_2$: C, 59.52; H, 4.59. Found: C, 59.50; H, 4.45.

[Cu(tmbp)(PPh$_3$)$_2$][BF$_4$] 5

Triphenylphosphine (0.58 g, 2.2 mmol) was added to a solution of complex **2** (0.48 g, 1 mmol) in CH_2Cl_2 (20 mL). After 10 min of stirring, the solvent was evaporated yielding a yellow solid which was washed twice with hexane (30 mL) to remove the excess PPh_3. The resulting powder was then dissolved in CH_2Cl_2 (30 mL) and filtered. After evaporation and drying, complex **5** was recovered as a yellow solid. Yield: 0.87 g (95%).

^{31}P NMR (CD_2Cl_2): δ 154.15 (pt, A_2X_2, ΣJ (P-P) = 44.85, P of tmbp), 7.26 (pt, A_2X_2, P of PPh_3).

^1H NMR (CD_2Cl_2): δ 2.31 (s, 6H, Me of tmbp), 2.45 (s, 6H, Me of tmbp), 7.05–7.40 (m, 30H, CH of C_6H_5), 7.83 (pt, AA'XX', 2H, ΣJ (H-P) = 31.60, $H_{6,6'}$ of tmbp), 8.31 (pt, AA'XX', 2H, ΣJ (H-P) = 10.17, $H_{3,3'}$ of tmbp).

^{13}C NMR (CD_2Cl_2): δ 23.60 (s, Me of tmbp), 24.25 (s, Me of tmbp), 129.70 (s, CH of C_6H_5), 131.35 (s, CH of C_6H_5), 133.70 (bs, $C_{3,3'}$ of tmbp), 134.0 (m, CH and Cq of C_6H_5), 142.60 (pt, AXX', ΣJ (C-P) = 21.65, $C_{4,4'}$ or $C_{5,5'}$), 147.0 (bs, $C_{6,6'}$), 147.75 (pt, AXX', ΣJ (C-P) = 13.85, $C_{4,4'}$ or $C_{5,5'}$), 160.55 (pt, AXX', ΣJ (C-P) = 29.30, $C_{2,2'}$).

Anal calc for $C_{50}H_{46}BCuF_4P_4$: C, 65.19; H, 5.03. Found: C, 65.35; H, 5.09.

[Cu(tmbp)(dppe)][BF$_4$] 6

1,2-Bis(diphenylphosphino)ethane (0.40 g, 1 mmol) was added to a solution of complex **2** (0.48 g, 1 mmol) in CH_2Cl_2 (20 mL). After 10 min stirring, CH_2Cl_2 was evaporated and the resulting yellow powder was washed with hexane

Table I. Crystal data for **5** and **8**.

Compound	**5**	**8**
Formula	$C_{56}H_{51}BCuF_4P_4$	$C_{24}H_{24}BCuF_4N_2P_2$
Space group	$C2/c$	$P2_1/n$
a (Å)	14.451(1)	13.110(1)
b (Å)	24.834(2)	8.299(1)
c (Å)	14.718(1)	22.611(2)
β (°)	109.61(2)	101.12(2)
V (Å^3)	4975.5(1.4)	2413.87(77)
Z	4	4
$d$calc (g/cm^3)	1.333	1.521
μ (cm^{-1})	6.2	10.8
F(000)	2068	1128
Maximum 2θ	60.0	60.0
No of refl measured	7652 total, 7243 unique	7789 total, 7039 unique
Reflections included	3681 with $Fo^2 > 3.0\sigma(Fo^2)$	4634 with $Fo^2 > 3.0\sigma(Fo^2)$
Parameters refined	318	307
Unweighted agreement factor	0.065	0.060
Weighted agreement factor	0.092	0.086
Instrument instability factor, p	0.08	0.08
GOF	1.62	1.76
Convergence largest shift/error	0.01	0.01

(30 mL). After being dissolved in CH_2Cl_2 (30 mL), complex **6** was filtered. Compound **6** was obtained as an orange solid after evaporation of the solvent and drying. Yield: 0.76 g (95%).

^{31}P NMR (CD_2Cl_2): δ 154.70 (bs, P of tmbp), 8.06 (bs, P of dppe).

^1H NMR (CD_2Cl_2): δ 2.38 (s, 6H, Me of tmbp), 2.47 (s, 6H, Me of tmbp), 2.67 (pt, 4H, AA'XX', ΣJ (H-P) = 12.58, CH_2 of dppe), 7.05–7.58 (m, 20H, CH of C_6H_5), 7.90 (pt, 2H, AA'XX', ΣJ (H-P) = 30.42, $H_{6,6'}$ of tmbp), 8.40 (m, 2H, $H_{3,3'}$).

^{13}C NMR ($CDCl_3$): δ 23.75 (s, Me of tmbp), 24.40 (s, Me of tmbp), 26.40 (pt, AXX', ΣJ (C-P) = 38.60, CH_2 of dppe), 129.95 (m, CH of C_6H_5), 131.05 (bs, $C_{3,3'}$ of tmbp), 131.70 (m, CH of C_6H_5), 133.10 (m, CH and Cq of C_6H_5), 141.95 (pt, AXX', ΣJ (C-P) = 22.20, $C_{4,4'}$ or $C_{5,5'}$), 146.20 (bs, $C_{6,6'}$), 147.60 (pt, AXX', ΣJ (C-P) = 13.50, $C_{4,4'}$ or $C_{5,5'}$), 159.75 (pt, AXX', ΣJ (C-P) = 34.0, $C_{2,2'}$).

Anal calc for $C_{40}H_{40}BCuF_4P_4$: C, 60.43; H, 5.07. Found: C, 60.42; H, 5.06.

[Cu(tmbp)(Py)₂][BF₄] 7

Pyridine (0.63 g, 8 mmol) was added to a solution of complex **2** (0.48 g, 1 mmol) in CH_2Cl_2 (20 mL). As pyridine was added the color of the solution changed from yellow to dark orange. Hexane (50 mL) was then added to precipitate complex **7** after the evaporation of half of the solvent. After elimination of the hexane/CH_2Cl_2 solution containing the excess pyridine, the resulting powder was dissolved in CH_2Cl_2 (15 mL). After filtration on celite, evaporation of the solvent and drying, complex **7** was isolated as an orange powder. Yield: 0.47 g (85%).

^{31}P NMR (CD_2Cl_2): δ 148.75.

^1H NMR ($CDCl_3$): δ 2.43 (pt, 6H, AA'XX', ΣJ (H-P) = 4.70, Me of tmbp), 2.48 (s, 6H, Me of tmbp), 7.26–8.0 (m, 10H, CH of C_5H_5N), 8.15 (pt, 2H, AA'XX', ΣJ (H-P) = 10.17, $H_{3,3'}$ of tmbp), 8.30 (pt, 2H, AA'XX', ΣJ (H-P) = 31.25, $H_{6,6'}$).

^{13}C NMR ($CDCl_3$): δ 23.30 (s, Me of tmbp), 27.55 (s, Me of tmbp), 125.75 (bs, CH of C_5H_5N), 135.35 (bs, $C_{3,3'}$ of tmbp), 138.25 (s, CH of C_5H_5N), 140.85 (pt, AXX', ΣJ (C-P) = 21.40, $C_{4,4'}$ or $C_{5,5'}$), 145.45 (bs, $C_{6,6'}$ of tmbp), 146.95 (pt, AXX', ΣJ (C-P) = 14.40, $C_{4,4'}$ or $C_{5,5'}$), 150.40 (s, CH of C_5H_5N), 160.80 (pt, AXX', ΣJ (C-P) = 19.85, $C_{2,2'}$).

Complex **7** was too labile to give satisfactory microanalytical data.

Polymer chain [Cu(tmbp)(bpy)][BF₄] 8

Biphosphinine **1** (0.74 g, 3 mmol) and 2,2'-bipyridine (0.47 g, 3 mmol) were added to a solution of complex $[Cu(MeCN)_4][BF_4]$ (0.94 g, 3 mmol) in CH_2Cl_2 (75 mL) at room temperature. After 5 min stirring, a yellow powder started to precipitate. The mixture was stirred for an additional 30 min and hexane (30 mL) was added. After filtration under nitrogen, the powder thus obtained was washed successively with hexane (30 mL), ether (30 mL). After drying, polymer **8** was recovered as a yellow solid which was crystallized in CH_2Cl_2. Yield: 1.32 g (80%).

^{31}P NMR ($CDCl_3$): δ 157.74.

^1H NMR ($CDCl_3$): δ 2.42 (s, 6H, 2 × Me of tmbp), 2.45 (t, 6H, J (H-P) = 5.05, Me of tmbp), 7.10 (m, 2H, H of bpy), 7.55 (m, 2H, H of bpy or H of tmbp), 7.9–8.5 (m, 8H, H of bpy and H of tmbp).

Anal calc for $C_{24}H_{24}BCuF_4N_2P_2$: C, 52.15; H, 4.38. Found: C, 52.10; H, 4.56.

X-ray structure determinations for 5 *and* 8

Crystals of **5** were grown by diffusion of hexane in a chlorobenzene solution of the compound. Compound **8** was recrystallized from a dichloromethane solution. Both data sets were collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo$K\alpha$ radiation (λ = 0.71073 Å) and a graphite monochromator. The crystal structures were solved and refined using the Enraf Nonius MOLEN package and were solved by direct methods using SIR92. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. Relevant crystal and refinement parameters are assembled in table I.

Supplementary material

For $C_{56}H_{51}BCuF_4P_4$ (complex **5**) and $C_{24}H_{24}BCuF_4N_2P_2$ (complex **8**).

– Table of experimental details (1 page for **5** and 1 page for **8**)

– Table of bond distances in Å (1 page for **5** and 1 page for **8**)

– Table of bond angles in degrees (2 pages for **5** and 1 page for **8**)

– Table of positional parameters and their estimated standard deviations (2 pages for **5** and 2 pages for **8**)

– Table of refined displacement parameter expression-β's (2 pages for **5** and 2 pages for **8**)

– Values of $10 * F_{\text{obs}}$ and $10 * F_{\text{calc}}$ (21 pages for **5** and 27 pages for **8**).

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90430 and is available on request from the Document Supply Center

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