

Chemistry of Bridging Phosphanes: Cu^I Dimers Bearing 2,5-Bis(2-pyridyl)phosphole Ligands

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Abstract: Bis(2-pyridyl)phosphole **1** reacted with Cu^I sources giving rise to dicationic or neutral dimers **2,3**. In these derivatives, **1** acts as a 1κN:1,2κP:2κN donor with a symmetrically bridging P centre. X-ray diffraction studies of these species revealed no constraint due to the unusual coordination mode of the P donor. A comparative study with a monometallic Cu^I complex in which **1** acts as a P,N chelate is presented. The acetonitrile ligands of the dicationic complex **2** can be displaced by a variety of donors. Bipyridine (bipy) acts as a chelating donor, while

1,1'-bis(diphenylphosphino)methane (dppm) and bis(2-pyridyl)phosphole **1** behave as bridging ligands. By using dppm and **1**, the complexes arising from the stepwise displacement of the acetonitrile ligands of complex **2** can be isolated. X-ray diffraction studies performed on these novel complexes revealed that the P centre can easily switch from a bridging to a semibridg-

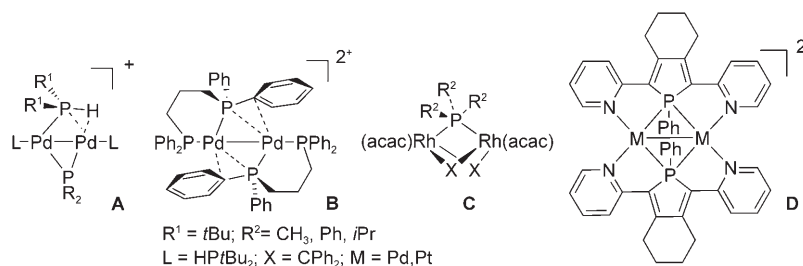
ing coordination mode. Of particular interest, within the same unit cell, complexes with P centres exhibiting bridging and semibridging coordination modes are observed. This switching can be induced by weak effects such as a different conformation of the incoming ligand. Cu^I dimers assembled by **1** are air-stable derivatives that are not water sensitive. Hydrolysis of the PF₆⁻ counterion occurs under drastic conditions and results in the formation of a PO₂F₂ fragment coordinated to a Cu^I-**1** fragment.

Keywords: bridging ligands • coordination modes • copper • P ligands • phosphorus heterocycles

Introduction

The versatility of a ligand in coordination chemistry results largely from its ability to adopt a variety of coordination modes. One prototypical example is carbon monoxide, which is able to stabilise a large variety of metal centres and clusters through terminal, semibridging and symmetrical coordination modes.^[1] In contrast, tertiary phosphanes PR₃, which are some of the most widely used donors in coordination chemistry, represent a remarkable counter-example in that they act almost exclusively as terminal ligands.^[2] Semibridging

phosphane ligands have appeared sporadically in the literature since the early 1990s,^[3] and it is significant that this bonding mode is always enforced by an agostic interaction involving a P–H or a P–C_{sp²} moiety (complexes **A** and **B**). The first example of a symmetrically bridging phosphane



was found in Rh^I dimers of type **C** as recently as 2000.^[4] This seminal discovery was a breakthrough in coordination chemistry, since binucleating ligands potentially allow the synthesis of polynuclear complexes that are of great interest in many fields, such as catalysis, bioinorganic chemistry and materials sciences.^[5] The only other examples of a bridging phosphane known to date involve phospholes in Pd^I-Pd^I and mixed Pd^I-Pt^I complexes **D**.^[6a-c] The chemistry of bridg-

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ing phosphanes is therefore still in its infancy.^[2a-c] Thus there is a need for the development of a series of new bridging phosphane complexes in order to elucidate their coordination behaviour and to study their chemical stability.^[7] In this paper, we describe the synthesis, structural characterisation and reactivity of a family of dimetallic Cu^I complexes containing bridging phosphane centres. This novel series reveals important new facets of bridging P donor chemistry. We show that bridging phosphanes can stabilise d¹⁰ metal dimers (**C** and **D** both feature d⁹ centres), that they can tolerate ligand exchange reactions (a key process in coordination chemistry) and that there is a continuum between bridging and semibringing coordination modes (a well-known behaviour of typical bridging ligands such as CO).^[1] These results, which have been partially reported in a preliminary communication,^[6d] constitute an important step to establishing phosphanes as versatile binucleating ligands.

Results and Discussion

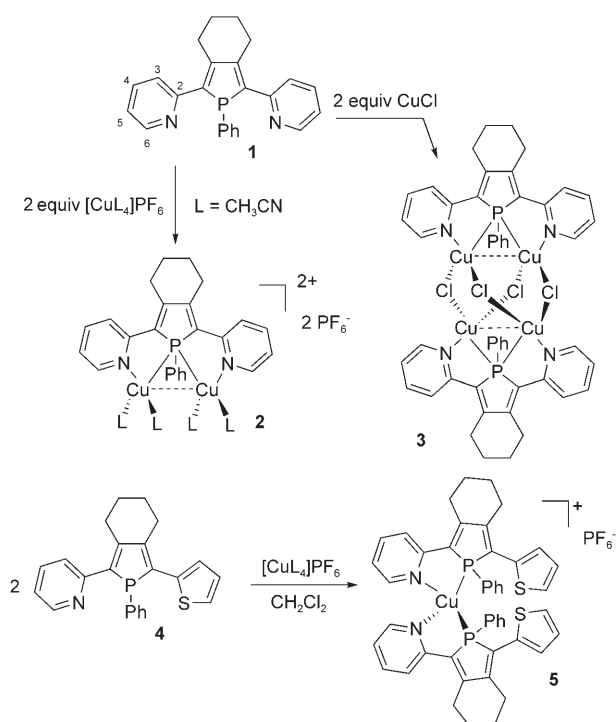
Synthesis of Cu^I dimers bearing a bridging 1-phenyl-2,5-bis(2-pyridyl)phosphole ligand: The ability of 1-phenyl-2,5-bis(2-pyridyl)phosphole (**1**;^[8] Scheme 1) to act as an assembling N,P,N donor has already been shown by the synthesis of dimers **D** based on square-planar d⁹-metal centres.^[6a-c] The reactivity of **1** towards tetrahedral d¹⁰-Cu^I ions was investigated to evaluate its potential for stabilizing dimetallic species based on metals with different electron counts and coordination geometries. The reaction of one equivalent of phosphole **1** with two equivalents of [Cu(CH₃CN)₄]PF₆ in

CH₂Cl₂ or THF at room temperature afforded the bimetallic complex **2** (Scheme 1) in 95% yield. Remarkably, this Cu^I complex is air stable both in the solid state and in solution (THF, CH₂Cl₂). Its room temperature ³¹P{¹H} NMR spectrum, recorded in CD₂Cl₂, exhibits a broad singlet at δ = -0.1 ppm (ν_{1/2} = 85 Hz) in addition to the PF₆⁻ ion signals. This signal is shifted to low frequencies relative to that of the free ligand **1** (a sharp singlet at δ = +11.7 ppm), clearly indicating a coordination of the P atom of **1** to the Cu^I metal ions. Integration of the ¹H NMR spectrum showed that complex **2** contains one molecule of **1** and four acetonitrile ligands. The simplicity of the ¹³C{¹H} NMR spectrum is indicative of a symmetrical structure with one set of signals assignable to the phosphole-based ligand **1** and one set to the CH₃CN donors. Interestingly, the ¹H and ¹³C NMR signals of the C⁶H pyridine fragments are different from those observed for the free ligand **1** (Table 1) suggesting a coordi-

Table 1. Selected spectroscopic data for ligand **1** and Cu^I dimers **2**, **3** and **6–10** in CD₂Cl₂.^[a]

	δ ³¹ P (ν _{1/2})	δ ¹ H H ⁶ _{py}	δ ¹³ C C ² _{py} –C ⁶ _{py}
1	+11.7 (<3 Hz)	8.50	155.9–149.4
2	-0.1 (85 Hz)	8.63	152.1–150.3
3	+0.1 (220 Hz)	8.85	–
6	+3.0 (91 Hz)	8.08	151.9–149.7
7	+13.7 (μ-P); -1.6	8.31	152.9–150.0
8	+8.9 (117 Hz)	8.43	152.9–151.9
9	+10.7 (μ-P); -2.7; -7.0	8.12	152.2–150.5
10	+12.0 (103 Hz); +4.9 (290 Hz)	8.40	150.2–149.8

[a] See Scheme 1 for the numbering of the pyridyl moiety.



Scheme 1. Synthesis of Cu^I complexes **2**, **3** and **5**.

nation of the pyridyl moieties to the Cu^I centres. Hence, these data, obtained in solution, suggest that ligand **1** acts as a N,P,N donor. This assumption was confirmed by a single-crystal X-ray diffraction study (Tables 2 and 3).^[6d] Indeed, the dication of **2** (Scheme 1) contains two Cu^I metal centres tethered by one phosphole ligand **1**, which acts as a 6-electron μ-1κN:1,2κP:2κN donor. Each metal centre also bears two acetonitrile ligands. The Cu^I atoms have a distorted tetrahedral coordination sphere as a result of the small bite angle of the P,N chelates (N–Cu–μ-P, 79.27(8)–86.67(6)°, Table 4). As observed for complex **D** (M = Pd), the two five-membered metallacycles of **2** have a slightly deformed envelope conformation, with the Cu, N and the two inter-ring C atoms being almost coplanar (dihedral angles < 8.2°) and the P atoms lying out of these planes (dihedral NCCP and CNCuP angles : 23.4, 23.7° and 17.9, 26.4°). Likewise, the dihedral angles between the coordinated pyridine and phosphole moieties (28.6 and 31.2°, respectively) are comparable for **2** and **D** (M = Pd). The geometric data of the bis(2-pyridyl)phosphole moiety are unremarkable and very similar to those observed for the free derivative **1**^[8] or in complexes **D**^[6a-c] (Table 5). The metal–metal distance in **2** (2.568(10) Å) is fairly short suggesting metallophilic interactions between the two d¹⁰-metal centres.^[9] The two Cu–N–(pyridine) bond lengths are essentially equal and the σ³-P

Table 2. Structure determination summary of complexes **2**, **3** and **5–7**.

	2	3 ·5 CH ₂ Cl ₂	5 ·2 CH ₂ Cl ₂	6 ·CH ₂ Cl ₂	7a ·CH ₂ Cl ₂	7b ·CH ₂ Cl ₂
formula	C ₃₂ H ₃₃ Cu ₂ - F ₁₂ N ₆ P ₃	C ₅₃ H ₅₂ Cl ₁₄ Cu ₄ - N ₄ P ₂	C ₄₈ H ₄₄ Cl ₄ Cu- F ₆ N ₂ P ₃ S ₂	C ₄₅ H ₃₉ Cl ₂ Cu ₂ - F ₁₂ N ₆ P ₃	C ₅₄ H ₅₁ Cl ₂ Cu ₂ - F ₁₂ N ₄ P ₃	C ₅₄ H ₅₁ Cl ₂ Cu ₂ - F ₁₂ N ₄ P ₃
<i>M_r</i>	949.63	1557.39	1125.22	1182.71	1336.82	1336.82
<i>T</i> [K]	120(2)	120(2)	120(2)	293(2)	293(2)	120(2)
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	<i>C</i> ₂	<i>P</i> ₂	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	22.409(4)	15.681(2)	8.653(2)	9.693(5)	20.981(5)	10.889(1)
<i>b</i> [Å]	14.915(3)	11.990(2)	17.088(2)	11.260(5)	11.351(5)	13.408(2)
<i>c</i> [Å]	13.606(3)	16.355(2)	18.787(3)	21.865(5)	25.467(5)	19.672(2)
α [°]	90	90	98.406(1)	92.513(5)	90	90.980(6)
β [°]	120.228(8)	91.573(1)	101.868(2)	90.901(5)	107.898(5)	93.142(6)
γ [°]	90	90	101.570(2)	95.364(5)	90	99.864(5)
<i>V</i> [Å ³]	3929(2)	3073.8(1)	2611.9(2)	2373.2(17)	5772(3)	2824.4(18)
<i>Z</i>	4	2	2	2	4	2
colour	yellow	red	orange	orange	yellow	orange
crystal size [mm]	0.35 × 0.20 × 0.15	0.30 × 0.20 × 0.20	0.30 × 0.10 × 0.04	0.50 × 0.50 × 0.50	0.30 × 0.10 × 0.05	0.10 × 0.10 × 0.10
ρ_{calcd} [Mg m ⁻³]	1.605	1.683	1.431	1.655	1.538	1.572
<i>F</i> (000)	1912	1564	1148	1192	2712	1356
μ (MoK α) [cm ⁻¹]	1.294	2.066	0.851	1.199	1.048	1.070
index ranges	-29 ≤ <i>h</i> ≤ 29 -19 ≤ <i>k</i> ≤ 19 -17 ≤ <i>l</i> ≤ 17	-20 ≤ <i>h</i> ≤ 20 -15 ≤ <i>k</i> ≤ 15 -21 ≤ <i>l</i> ≤ 21	-10 ≤ <i>h</i> ≤ 11 -22 ≤ <i>k</i> ≤ 21 -24 ≤ <i>l</i> ≤ 24	-12 ≤ <i>h</i> ≤ 12 -14 ≤ <i>k</i> ≤ 14 -28 ≤ <i>l</i> ≤ 28	-27 ≤ <i>h</i> ≤ 27 -13 ≤ <i>k</i> ≤ 14 -33 ≤ <i>l</i> ≤ 32	-13 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 17 -25 ≤ <i>l</i> ≤ 25
θ range [°]	3.05–27.48	3.26–27.43	2.92–27.58	2.91–27.50	2.65–27.48	3.00–27.51
reflins collected	26 988	13 476	21 191	16 775	24 751	23 883
independent reflns	8782	13 463	11 938	10 735	13 208	12 882
reflections [<i>I</i> > 2 σ (<i>I</i>)]	6750	12 702	7222	8937	10 902	10 689
data/restraints/parameters	8782/2/547	13 463/2/695	11 938/0/596	10 735/0/631	13 208/0/734	12 882/0/715
goodness-of-fit on <i>F</i> ²	1.023	1.051	1.022	1.022	1.026	1.051
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0483 <i>wR</i> 2 = 0.1151	<i>R</i> 1 = 0.0501 <i>wR</i> 2 = 0.1289	<i>R</i> 1 = 0.0796 <i>wR</i> 2 = 0.2173	<i>R</i> 1 = 0.0401 <i>wR</i> 2 = 0.972	<i>R</i> 1 = 0.0489 <i>wR</i> 2 = 0.1307	<i>R</i> 1 = 0.0401 <i>wR</i> 2 = 0.1027
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0742 <i>wR</i> 2 = 0.1323	<i>R</i> 1 = 0.0542 <i>wR</i> 2 = 0.1334	<i>R</i> 1 = 0.1297 <i>wR</i> 2 = 0.2555	<i>R</i> 1 = 0.0520 <i>wR</i> 2 = 0.1045	<i>R</i> 1 = 0.0614 <i>wR</i> 2 = 0.1410	<i>R</i> 1 = 0.0513 <i>wR</i> 2 = 0.1105
<i>S</i> ^[a]	0.515(13)	0.510(10)	–	–	–	–
largest diff peak/hole [e Å ⁻³]	0.377/–0.332	0.988/–0.881	0.803/–0.733	0.886/–0.768	1.482/–0.912	0.656/–0.794

[a] *S* = absolute structure parameter.

atom presents an almost symmetrical bridging coordination mode ($\Delta(\text{P–Cu}) = 0.010(2)$ Å; Table 4). Note that the Cu–N bond lengths are significantly shorter (ca. 0.13 Å) in Cu^I derivative **2** compared to Pd^I dimer **D** whereas the metal– μ -P separations lie in the same range (**2**: 2.314(1)–2.324(1) Å; **D**: 2.349(2)–2.358(2) Å). As expected for a symmetrically bridging phosphane ligand, the two P–Cu–Cu angles are almost equivalent (56.18(4), 56.57(4)°). Remarkably, the geometric features of **2** are similar to those observed for Pd^I dimer **D**^[6a,c] in spite of the different geometries (Pd^I: square-planar; Cu^I: tetrahedral) and atomic radii of the metal centres. This similarity suggests that the structural parameters of metal dimers assembled by bis(2-pyridyl)phosphole ligand **1** featuring a bridging P centre are imposed by this rigid N,P,N pincer.

1-Phenyl-2,5-bis(2-pyridyl)phosphole (**1**) is also able to stabilise neutral Cu^I dimers as illustrated by the synthesis of complex **3** (Scheme 1). This derivative was obtained in 82% yield by reacting **1** with two equivalents of CuCl in CH₂Cl₂. Its ³¹P{¹H} and ¹H NMR data are essentially comparable to those of dimer **2** (Table 1) and this complex was characterised by an X-ray diffraction study (Table 2, Figure 1). Here also, derivative **1** acts as a 6-electron μ -1 κ N:1,2 κ P:2 κ N donor with the P atoms in a bridging coordination mode

(P–Cu distances: 2.273(2)–2.326(2) Å; P–Cu–Cu angles, 54.63(4)–56.59(4)°, Table 4). The geometry around the Cu^I atoms is a distorted tetrahedron and the Cu–Cu distances (2.566(1) and 2.598(1) Å) lie in the range of those observed for complex **2** (Table 4). The metal centres of the Cu₄Cl₄ core have a distorted tetrahedral geometry (angles: Cl–Cu–Cl, 101.3–106.4°; N–Cu–P, 83.38–85.93°) and the chlorine atoms bridge two Cu^I atoms with classic Cu–Cl–Cu angles (85.5–88.2°) and Cu–Cl bond lengths (2.326(2)–2.374(1) Å).^[10a–c] The Cu₄Cl₄ framework of **3** is unusual, since this fragment generally adopts a cubane skeleton with μ^3 -Cl atoms.^[9b,10d–g] The best way to describe the core of the tetranuclear species **3** is to consider all the μ^2 -bridging ligands, that is, the Cl and P atoms. The Cu₄Cl₄P₂ fragment thus displays an adamantane-type framework (Figure 1, right), which is distorted due to the acute Cu–Cl–Cu and Cu–P–Cu angles.

With the aim of evaluating the impact of the bridging coordination mode of the P donor on the Cu^I coordination sphere, the synthesis of the monometallic Cu^I complex **5** featuring bidentate 2-(2-pyridyl)phosphole ligands was undertaken (Scheme 1). This compound was obtained in quantitative yield by reacting two equivalents of 2-(2-pyridyl)-5-(2-thienyl)phosphole (**4**)^[6b] with [Cu(CH₃CN)₄]PF₆ in

Table 3. Structure determination summary of complexes **8–11**.

	8 ·CH ₂ Cl ₂	9a ·2 CH ₂ Cl ₂ ·H ₂ O	(9b) ₂ ·CH ₂ Cl ₂	(9c) _{1.5} ·2 CH ₂ Cl ₂	10 ·2 THF	(11) ₂ ·2.5 THF·2 H ₂ O
formula	C ₅₃ H ₅₀ Cl ₂ Cu ₂ - F ₁₂ N ₆ P ₄	C ₇₆ H ₇₁ Cl ₄ Cu ₂ - F ₁₂ N ₂ OP ₇	C ₁₄₉ H ₁₃₂ Cl ₂ Cu ₄ - F ₂₄ N ₄ P ₁₄	C _{112.5} H _{100.5} Cl ₄ Cu ₃ - F ₁₈ N ₃ P _{10.5}	C ₈₀ H ₇₉ Cu ₂ - F ₁₂ N ₆ O ₂ P ₅	C ₁₀₅ H ₉₄ Cu ₄ - F ₁₆ N ₄ O _{8.5} P ₁₀
<i>M_r</i>	1320.85	1742.02	3193.23	2494.06	1666.42	2416.21
<i>T</i> [K]	120(2)	100(2)	100(2)	100(2)	120(2)	120(2)
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>Pcab</i>	<i>P2₁/n</i>	<i>P1</i>	<i>P2₁/n</i>	<i>P2₁/a</i>	<i>P2₁/n</i>
<i>a</i> [Å]	14.944(1)	14.642(1)	12.8315(6)	12.1319(6)	19.482(3)	17.373(2)
<i>b</i> [Å]	24.266(3)	28.532(2)	22.5160(12)	46.3538(19)	18.725(3)	17.399(2)
<i>c</i> [Å]	31.841(4)	17.804(2)	24.2608(12)	35.5690(18)	23.276(3)	35.192(4)
<i>α</i> [°]	90	90	91.490(2)	90	90	90
<i>β</i> [°]	90	93.297(4)	91.529(3)	95.252(3)	113.841(7)	93.312(5)
<i>γ</i> [°]	90	90	99.838(2)	90	90	90
<i>V</i> [Å ³]	11 547(5)	7426(4)	6900.4(6)	19918.6(16)	7767(3)	10 620(5)
<i>Z</i>	8	4	2	8	4	4
colour	orange	yellow	yellow	yellow	red	orange
crystal size [mm]	0.04 × 0.04 × 0.01	0.30 × 0.10 × 0.10	0.30 × 0.02 × 0.02	0.40 × 0.03 × 0.02	0.10 × 0.05 × 0.02	0.35 × 0.30 × 0.20
<i>ρ</i> _{calcd} [Mg m ⁻³]	1.520	1.558	1.537	1.663	1.425	1.511
<i>F</i> (000)	5360	3552	3260	10168	3432	4922
<i>μ</i> (MoK _α) [cm ⁻¹]	1.021	0.945	0.896	1.000	0.730	1.027
index ranges	-18 ≤ <i>h</i> ≤ 18, -30 ≤ <i>k</i> ≤ 30 -38 ≤ <i>l</i> ≤ 38	-19 ≤ <i>h</i> ≤ 16, -33 ≤ <i>k</i> ≤ 37, -23 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 16, -29 ≤ <i>k</i> ≤ 29, -31 ≤ <i>l</i> ≤ 27	-12 ≤ <i>h</i> ≤ 13 -51 ≤ <i>k</i> ≤ 50 -42 ≤ <i>l</i> ≤ 42	-24 ≤ <i>h</i> ≤ 24 -23 ≤ <i>k</i> ≤ 23 -29 ≤ <i>l</i> ≤ 29	-22 ≤ <i>h</i> ≤ 22 -22 ≤ <i>k</i> ≤ 22 -45 ≤ <i>l</i> ≤ 45
<i>θ</i> range [°]	3.05–27.48	1.35–27.57	0.84–27.55	0.72–25.28	2.09–27.07	2.92–27.51
reflins collected	18 589	73 974	96 203	149 054	33 280	36 066
independent reflns	10 592	17 035	31 403	30 975	17 054	23 007
reflections [<i>I</i> > 2σ(<i>I</i>)]	7374	9727	20 078	18 281	7131	13 334
data/restraints/parameters	10 592/0/769	17 035/0/936	31 403/0/1774	30 975/0/2708	17 054/0/935	23 007/0/1365
goodness-of-fit on <i>F</i> ²	1.069	0.887	1.024	1.036	0.958	1.006
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0621 <i>wR</i> 2 = 0.1494	<i>R</i> 1 = 0.0493 <i>wR</i> 2 = 0.1132	<i>R</i> 1 = 0.0459 <i>wR</i> 2 = 0.1124	<i>R</i> 1 = 0.0750 <i>wR</i> 2 = 0.1906	<i>R</i> 1 = 0.0670 <i>wR</i> 2 = 0.1634	<i>R</i> 1 = 0.0668 <i>wR</i> 2 = 0.1399
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0941 <i>wR</i> 2 = 0.1664	<i>R</i> 1 = 0.0928 <i>wR</i> 2 = 0.1226	<i>R</i> 1 = 0.0965 <i>wR</i> 2 = 0.1500	<i>R</i> 1 = 0.1421 <i>wR</i> 2 = 0.2277	<i>R</i> 1 = 0.1773 <i>wR</i> 2 = 0.2291	<i>R</i> 1 = 0.1361 <i>wR</i> 2 = 0.1696
largest diff peak/hole [e Å ⁻³]	0.327/–0.305	1.362/–0.1008	1.342/–0.948	2.697/–1.360	0.497/–0.423	0.919/–0.673

CH₂Cl₂; crystals suitable for an X-ray diffraction study were obtained (Table 2, Figure 2). The angles and bond lengths of the coordinated (2-pyridyl)phosphole fragments are comparable for dimers **2** and **3** and monometallic species **5**, indicating that the bridging coordination mode of the P centre does not perturb the ligand structure (Table 5). As observed for derivatives **2** and **3** (Table 4), the Cu^I centre of complex **5** has a distorted tetrahedral geometry with small P–Cu–N angles (85.80(10)° and 86.79(11)°). The Cu–N bond lengths are almost similar for all complexes (2.046(4)–2.061(4) Å); however, the P–Cu separations are markedly different. As expected, the P–Cu distances are significantly longer in dimers **2** and **3** (Table 4) featuring the bridging P donors than those measured in complex **5** (2.2734(13)–2.2850(14) Å). Note that the metal–P bond length difference between symmetrically bridging and nonbridging phosphane donors is more pronounced for Pd^I (ca. 0.1 Å)^[6a,c] than for Cu^I complexes (ca. 0.05 Å).

Phosphole **1** is thus able to assemble metal ions with different electronic counts and geometries (**D**, d⁹ square planar; **2** and **3**, d¹⁰ tetrahedral) in dimers featuring a bridging phosphane donor. The ease with which it acts as an assembling ligand is nicely illustrated by the fact that **2** and **3** are the first complexes in which the two metal centres are bridged by a phosphane donor and no other supporting li-

gands (**C** are triply bridged and **D** are doubly bridged). The next step in order to establish bridging phosphanes as versatile assembling ligands was to check whether classic reactions such as ligand exchange can be performed without fragmentation of the P-bridged dinuclear cores. Dimer **2** (Scheme 1) is a unique compound to elucidate this point, since, in contrast to previously synthesised metal dimers bearing bridging phosphanes, it possesses labile acetonitrile ligands. We have thus investigated the reaction of **2** with neutral bidentate ligands having different electronic (homo- and heteroditopic donors) and steric (1,3- and 1,4-chelates) properties.

Ligand exchange on dimer 2 involving 2,2'-bipyridine: To grasp the stability of the Cu₂^I-phosphole moiety in **2**, we have selected 2,2'-bipyridine (bipy) for comparison purposes, since this ligand is known to bind strongly to Cu^I giving rise to robust complexes.^[11] Upon addition of two equivalents of bipy to a solution of **2** in CH₂Cl₂ at room temperature, the yellow solution instantaneously turned red. The ³¹P{¹H} NMR spectrum of the crude reaction mixture showed a broad singlet at δ = 3.0 ppm with no signal at δ = 11.7 ppm from the free derivative **1**. After workup, the novel complex **6** (Scheme 2) was isolated as an air-stable red powder in 94% yield. Its ³¹P{¹H} NMR chemical shift (δ =

Table 4. Selected bonds lengths [\AA] and angles [$^\circ$] of the $\text{Cu}_2(\text{NPN})$ moieties of complexes **2**, **3** and **6–11**

	Cu– μ -P	Cu–N	Cu...Cu	N–Cu– μ -P	Cu– μ -P–Cu	μ -P–Cu–Cu
2	2.324(1) 2.314(1)	2.040(4) 2.041(5)	2.568(1)	85.29(1) 85.55(1)	67.25(4)	56.18(4) 56.57(4)
3 ^[a]	2.285(2) 2.299(2) 2.273(2) 2.326(2)	2.085(4) 2.078(4) 2.085(4) 2.099(4)	2.566(1) 2.598(1)	85.33(12) 84.92(12) 83.39(12) 84.43(13)	68.05(4) 68.78(4)	54.63(4) 56.59(4) 55.72(4) 56.23(4)
6	2.254(9) 2.269(8)	2.012(2) 2.054(2)	2.5231(8)	86.15(6) 86.67(6)	67.80(2)	55.81(2) 56.39(2)
7a	2.289(8) 2.522(8)	2.057(2) 2.061(2)	2.6696(7)	85.80(7) 82.78(7)	67.19(2)	52.24(2) 60.56(2)
7b	2.413(8) 2.402(8)	2.077(2) 2.062(2)	2.6822(9)	81.39(6) 82.79(6)	67.69(3)	55.95(2) 56.36(2)
8	2.293 (1) 2.386(1)	2.048(4) 2.043(4)	2.5552(8)	86.14(1) 82.85(1)	66.15(4)	55.17(3) 58.68(3)
9a	2.426(1) 2.557(1)	2.106(2) 2.073(3)	2.8329(9)	81.11(7) 79.56(7)	69.24(3)	53.20(3) 57.57(2)
9b ^[a]	2.500(1) 2.557(1) 2.535(1) 2.494(1)	2.110(3) 2.097(3) 2.084(3) 2.094(3)	2.8743(6) 2.9501(6)	76.35(8) 79.27(8) 79.45(8) 81.07(9)	69.25(3) 71.83(3)	54.45(2) 56.29(2) 53.43(2) 54.74(2)
9c ^[b]	2.427(2) 2.501(2) 2.252(2) 2.728(3) 2.668(2) 2.277(2)	2.075(6) 2.079(6) 2.122(7) 1.927(6) 1.959(6) 2.109(7)	2.8785(14) 2.9245(14)	77.74(2) 77.31(2) 80.2(2) 77.9(2) 77.7(2) 79.1(2)	71.46(6) 71.20(7) 69.72(7)	53.07(5) 55.48(6) 46.80(5) 62.00(7) 48.66(5) 61.62(6)
10	2.264(1) 2.559(1)	2.148(5) 2.055(5)	2.6204(9)	83.15(1) 78.22(1)	65.46(4)	51.84(4) 62.70(4)
11 ^[a]	2.365(2) 2.405(2) 2.384(2) 2.400(2)	2.049(4) 2.058(4) 2.065(4) 2.046(4)	2.6337(10) 2.6773(11)	84.33(11) 83.23(12) 83.09(11) 82.08(12)	67.01(4) 68.06(4)	55.78(3) 57.21(4) 55.70(4) 56.24(3)

[a] Two independent molecules in the unit cell. [b] Three independent molecules in the unit cell.

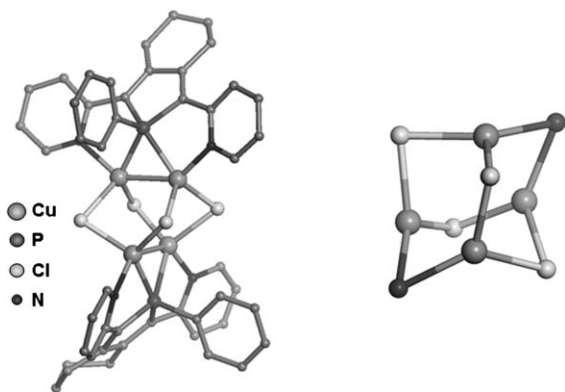
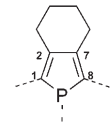


Figure 1. Left: Molecular structure of complex **3**. Hydrogen atoms have been omitted for clarity. Right: View of the $\text{Cu}_4\text{Cl}_4\text{P}_2$ cores.

Table 5. Selected bonds lengths [\AA] and angles [$^\circ$] of the bis(2-pyridyl)-phosphole moieties in free ligand **1** and complexes **2**, **3** and **5–11**.


	P–C ¹ P–C ⁸	C ¹ –C ²	C ² –C ⁷	C ⁷ –C ⁸	C ¹ –C _{py} C ⁸ –C _{py}	C ¹ –P–C ⁸
1	1.806(6) 1.806(6)	1.365(9)	1.478(9)	1.354(8)	1.466(9) 1.467(8)	90.5(3)
2	1.813(4) 1.822(4)	1.369(6)	1.463(7)	1.356(7)	1.453(6) 1.466(7)	90.5(2)
3 ^[a]	1.803(5) 1.830(5) 1.815(5) 1.814(5)	1.355(7) 1.375(7)	1.469(7) 1.472(7)	1.353(7) 1.362(7)	1.470(7) 1.471(7) 1.456(7) 1.478(7)	89.0(2) 89.7(2)
5 ^[a]	1.803(4) 1.814(5) 1.799(5) 1.821(4)	1.355(7) 1.373(6)	1.467(7) 1.460(6)	1.362(7) 1.364(7)	1.450(6) 1.464(6)	91.4(2) 91.1(2)
6	1.814(2) 1.822(2)	1.357(3)	1.479(3)	1.353(3)	1.462(3) 1.466(3)	90.14(10)
7a	1.808(3) 1.820(3)	1.359(4)	1.474(4)	1.363(4)	1.454(4) 1.461(4)	90.40(12)
7b	1.814(2) 1.823(2)	1.362(3)	1.479(3)	1.367(3)	1.465(3) 1.465(3)	90.45(10)
8	1.801(5) 1.811(5)	1.351(6)	1.465(7)	1.345(6)	1.464(6) 1.461(6)	90.5(2)
9a	1.810(3) 1.808(3)	1.358(4)	1.473(4)	1.356(4)	1.459(4)	90.84(14)
9b ^[a]	1.819(4) 1.821(4) 1.815(4) 1.808(4)	1.375(5) 1.364(5)	1.469(5) 1.467(5)	1.349(5) 1.367(5)	1.467(5) 1.468(5) 1.470(5) 1.455(5)	90.22(17) 90.29(16)
9c ^[b]	1.679(7) 1.801(8) 1.786(9) 1.772(9) 1.777(8) 1.786(8)	1.347(11) 1.345(12)	1.414(11) 1.409(13)	1.282(10) 1.346(12)	1.423(11) 1.380(10) 1.454(13) 1.413(12) 1.418(10) 1.432(11)	91.2(4) 88.6(4) 88.3(4)
10	1.814(6) 1.826(6)	1.361(8)	1.476(9)	1.371(8)	1.460(8) 1.453(9)	90.2(3)
11 ^[a]	1.810(5) 1.824(5) 1.802(5) 1.807(4)	1.363(6) 1.372(6)	1.480(6) 1.468(6)	1.357(6) 1.357(6)	1.470(6) 1.468(7) 1.466(6) 1.473(6)	90.5(2) 90.9(2)

[a] Two independent molecules in the unit cell. [b] Three independent molecules in the unit cell.

3.0 ppm) is in a similar range to that of **2** ($\delta = -0.1$ ppm), indicating that the P atom is still coordinated to the Cu^{I} centres. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, in addition to the signals expected for a coordinated ligand **1** in a symmetrical envi-

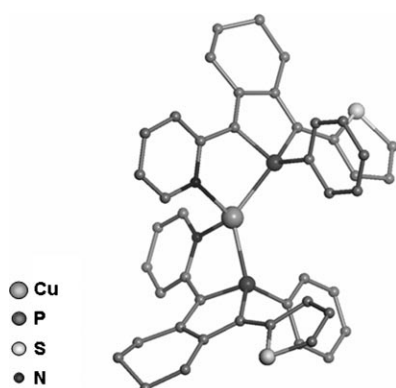
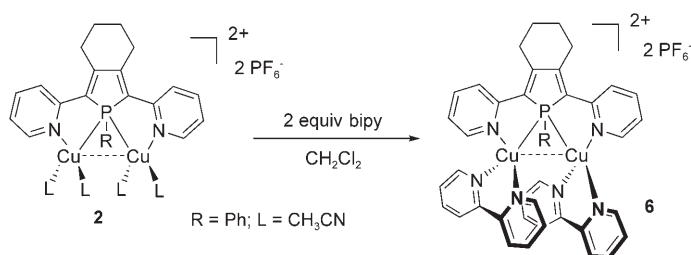


Figure 2. Molecular structure of cationic complex **5**. Hydrogen atoms have been omitted for clarity.



Scheme 2. Ligand exchange reaction leading to complex **6**.

ronment, singlets due to coordinated bipy are observed at classic chemical shifts.^[11] Notably no resonances assignable to acetonitrile ligands were observed. Altogether these spectroscopic data suggest that the labile acetonitrile ligands of **2** were simply substituted by bipy. This hypothesis was confirmed by a single-crystal X-ray diffraction study (Tables 2 and 4, Figure 3).

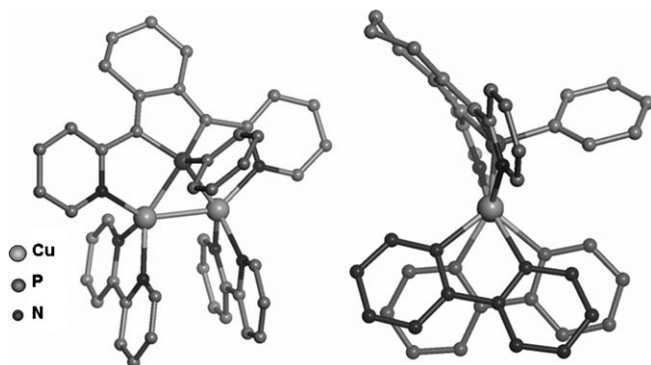
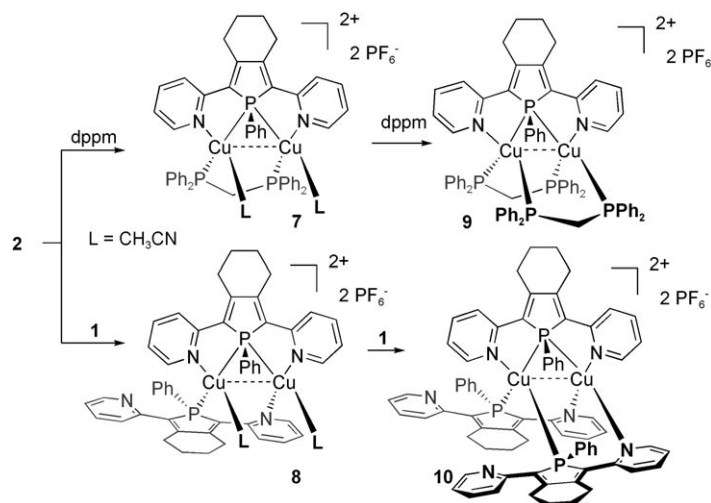


Figure 3. Molecular structure of dicationic complex **6**. Hydrogen atoms have been omitted for clarity.

The Cu^I dimer **6** still features one 2,5-bis(2-pyridyl)phosphole ligand **1** acting as a 6-electron $\mu\text{-}1\kappa\text{N}:1,2\kappa\text{P}:2\kappa\text{N}$ donor with the coordination sphere of the metal centers being completed by a chelating 2,2'-bipyridine ligand (Figure 3 left). The Cu^I ions have a distorted tetrahedral ge-

ometry due to the small bipyridine (80.25(8), 80.33(8)°) and (2-pyridyl)phosphole bite angles (Table 4). Note that the bipy ligands are slightly twisted (dihedral angles: 3.65(5), 7.09(6)°) and that they adopt a parallel-displaced arrangement (Figure 3 left) with short inter-ring distances (<3.4 Å) indicating $\pi\text{-}\pi$ interactions.^[12] The P atom adopts an almost symmetrical bridging coordination mode ($\Delta(\text{P-Cu}) = 0.015(1)$ Å, P-Cu-Cu angles, 55.72(4) and 56.23(4)°), but the Cu-P bond lengths are notably shorter than those of **2** (Table 4). The metal-metal distance (2.5231(8) Å) also decreases on going from dimer **2** to derivative **6** (Table 4). These data show that in spite of the rigidity of the tridentate N,P,N pincer **1**, the nature of the other Cu ligands can influence the geometric parameter of the Cu₂-phosphole core. The synthesis of **6** clearly demonstrates the robustness of bridging phosphanes as binucleating ligands, since bipy is known to exhibit a strong affinity for Cu^I ions. This result prompted us to investigate the reaction of **2** with other bidentate ligands with different bite angles and donor atoms such as bis-1,1'-(diphenylphosphino)methane (a 1,3-P,P chelate) and (2-pyridyl)phospholes (1,4-P,N chelates).

Ligand exchange on dimer 2 involving bis-1,1'-diphenylphosphinomethane (dppm) and bis(2-pyridyl)phosphole (1): Reaction of dppm with complex **2** in a 1:1 molar ratio afforded derivative **7**, which was isolated as an air-stable yellow powder in 91% yield (Scheme 3). Beside the resonances



Scheme 3. Ligand exchange reactions of phosphole-bridged Cu^I dimers.

due to the PF₆⁻ ion ($\delta = -144.3$ ppm, $J(\text{P},\text{F}) = 709.5$ Hz), the ³¹P{¹H} NMR spectrum of **7** in CD₂Cl₂ exhibits a doublet at $\delta = -1.6$ ppm and a triplet at $\delta = 13.7$ ppm with a coupling constant of 82.6 Hz. Selective ³¹P-decoupled ¹H experiments allowed unambiguous assignment of the signal at $\delta = -1.6$ ppm to the dppm ligand and that at $\delta = 13.7$ ppm to the phosphole ring. Hence, the phosphole ring is coupled with the two magnetically equivalent P atoms of dppm. The simplicity of the ¹H and ¹³C NMR spectra suggests a sym-

metric structure with one set of signals assignable to the bis(2-pyridyl)phosphole, the dppm and the acetonitrile ligands. Note that the ^1H NMR resonances of the dppm methylene protons are split into two groups of signals indicating that they are nonequivalent. The definitive proof for the proposed structure was given by a single-crystal X-ray diffraction study. A solution of **7** in CH_2Cl_2 was exposed to pentane vapours for three days leading to the formation of crystals with two different morphologies: pale yellow plates (major fraction) and pale orange prisms. The pale yellow plates of **7a** crystallised in the monoclinic space group $P2_1/n$, while the pale orange prisms of **7b** crystallised in the triclinic space-group $P\bar{1}$ (Table 2). In both cases, the asymmetric unit contains one dicationic bimetallic $[\{\text{Cu}^{\text{I}}(\mathbf{1})(\text{dppm})(\text{CH}_3\text{CN})_2\}_2]$ dimer, two hexafluorophosphate counterions and one disordered CH_2Cl_2 solvent molecule. In fact the dicationic complexes **7a** and **7b** (Figure 4) are simply con-

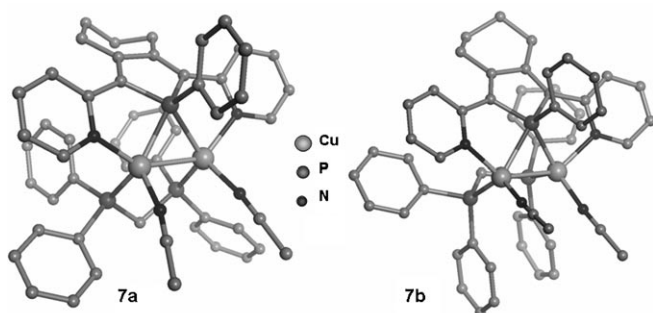


Figure 4. Molecular structure of dicationic complexes **7a** and **7b**. Hydrogen atoms have been omitted for clarity.

formers that differ only in the envelope conformations of the five membered $\text{Cu}_2\text{P}_2\text{C}$ rings formed by the $1\kappa\text{P}:2\kappa\text{P}$ -coordination of dppm. The methylene moiety of the dppm ligand is either *transoid* (**7a**) or *cisoid* (**7b**) with respect to the $\mu\text{-P}$ atom (Figure 5). In solution, it is likely that a very

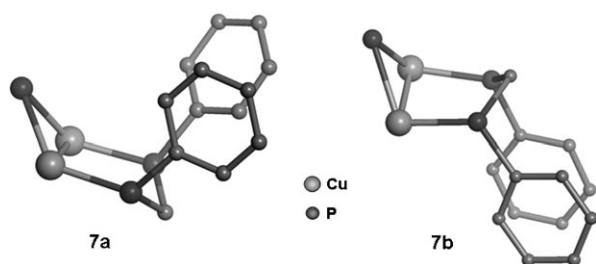


Figure 5. Views of the $\text{Cu}_2\text{P}_2\text{C}$ moieties of complexes **7a** and **7b**.

fast equilibrium between these two conformers takes place. The $\text{Cu}\cdots\text{Cu}$ distances of **7a** and **7b** are significantly longer than those recorded in complexes **2** and **6** (Table 4). This structural modification of the Cu_2 -phosphole core probably arises from the ring constraint associated with the formation of the five-membered $\text{Cu}_2\text{P}_2\text{C}$ metallacycle. The most impor-

tant information revealed by these solid state studies is that the coordination mode of the phosphole donor is different in conformers **7a** and **7b**. In **7b**, the P atom adopts a symmetrically bridging mode ($\Delta(\mu\text{-P-Cu})$: 0.01 Å), whereas in **7a** the P atom binds the metal centres unsymmetrically ($\Delta(\mu\text{-P-Cu})$: 0.23 Å; Table 4). Another structural parameter that clearly reflects these different coordination modes is the values of the P-Cu-Cu angles: they are similar for **7b**, but notably different for **7a** (Table 4). Note that the $\mu\text{-P-Cu}$ bond lengths in **7b** are much longer than those observed in complexes **2**, **3** and **6** (Table 4), confirming the impact of the remaining ligands on the geometry of the Cu_2 -phosphole core. The nonsymmetrical coordination mode of the P centre in dimer **7a** is particularly striking, since the gross structure of this complex is highly symmetric. Therefore, in spite of the rigid structure and tridentate coordination mode of the bis(2-pyridyl)phosphole **1**, the bridging P atom can adopt a semibringing coordination mode. This result highlights that the energy between symmetrical and nonsymmetrical bridging phosphane donors is rather small and that tiny steric effects, such as different conformations, can affect the local symmetry of a $\mu\text{-(PR}_3)_2\text{M}_2$ fragment.

The reactions of complex **2** with bipyridine (Scheme 2) and dppm (Scheme 3) revealed that, depending on its structure (1,4-N,N or 1,3-P,P donors), the incoming ligand can adopt either a chelating or a $1\kappa:2\kappa$ -bridging coordination mode. Therefore, it was interesting to investigate the behaviour of (2-pyridyl)phospholes which are known to act as 1,4-P,N donors (see complex **5**, Scheme 1).^[6b,c,13] The reaction of complex **2** with an equivalent of derivative **1** in CH_2Cl_2 at room temperature gives the complex **8**^[6d] (Scheme 3), which was isolated as an air-stable orange powder in 85% yield. The ambient-temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **8** display broad lines with one set of signals assignable to 1-phenyl-2,5-bis(2-pyridyl)phosphole and the acetonitrile ligands. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, in addition to the resonances due to the PF_6^- ion, a broad singlet is observed at $\delta = 8.9$ ppm ($\nu_{1/2} = 117$ Hz). On decreasing the temperature, this $^{31}\text{P}\{^1\text{H}\}$ NMR resonance broadened and shifted slightly to lower frequency with another resonance at $\delta = -0.4$ ppm appearing (Figure 6). Upon further cooling, the two resonances sharpened and shifted to higher and lower field, respectively (Figure 6) and at 193 K they were observed at $\delta = 7.1$ ppm and -0.3 ppm. These data clearly show that at room temperature, complex **8** exhibits fluxional behaviour. However, the multinuclear spectroscopic data do not allow a structure to be proposed and single crystals suitable for X-ray diffraction study were grown by diffusion of pentane in a solution of **8** in CH_2Cl_2 (Table 3).

Complex **8** is a Cu^{I} dimer two phosphole **1** ligands, one acting as a $\mu\text{-}1\kappa\text{N}:1,2\kappa\text{P}:2\kappa\text{N}$ donor and one acting as a $1\kappa\text{N}:2\kappa\text{P}$ chelate, and two acetonitrile ligands (Figure 7). The distance between the Cu centre and the nitrogen atom of the dangling free pyridine is 3.529 Å, ruling out any Cu-N interaction. The Cu-N (2.033(4) Å) and Cu-P (2.2499(13) Å) bond lengths associated with the $1\kappa\text{N}:2\kappa\text{P}$ -coordinated P,N-ligand **1** are unremarkable and very similar

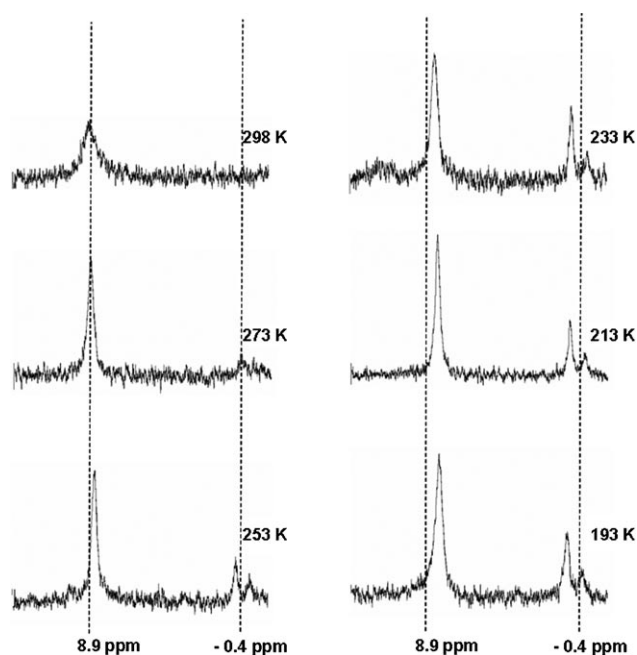


Figure 6. Temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex **8** in CD_2Cl_2 .

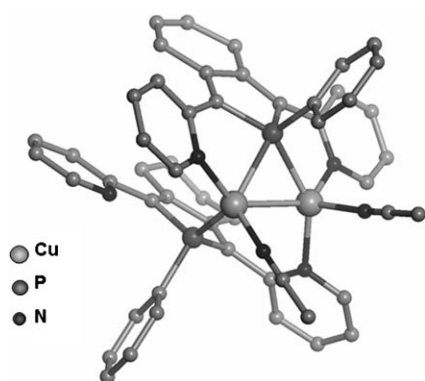
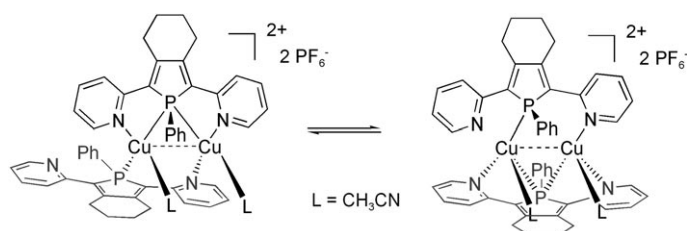


Figure 7. Molecular structure of dicationic complex **8**. Hydrogen atoms have been omitted for clarity.

to those of complex **5** (Scheme 1), with the exception of the torsion angle between the coordinated phosphole and pyridine rings, which is rather high (**5**, 27.1° ; **8**, 51.41°). It is very likely that the dynamic process observed in solution involves an intramolecular exchange between the pendant and coordinated pyridyl groups (Scheme 4). This degenerate equilibrium is very fast since it requires minimum reorganisation of the molecule due to the favourable pre-orientation of the free pyridine moiety (Figure 7). It should be noted that related hemilabile behaviour of ligand **1** has previously been encountered in monomeric Pd^{II} complexes.^[6b]

The $1\kappa\text{N}:2\kappa\text{P}$ coordination mode of **1**, which is unprecedented for (2-pyridyl)phosphole ligands, renders the two Cu^I atoms of **8** nonequivalent: Cu1 and Cu2 have “ PN_3 ” and “ P_2N_2 ” environments, respectively (Scheme 3, Figure 7). Up to now, bridging phosphane ligands have been described for



Scheme 4. Proposed ligand exchange process in complex **8**.

homodimers of high symmetry only (derivatives **C** and **D**). Complex **8** is thus the first nonsymmetrical homodimer bearing a bridging phosphane donor and this very interesting situation allows study of the impact of this local dissymmetry on the bonding situation of the $\mu\text{-P}$ centre. The $\text{Cu}^{\text{I}}\text{-Cu}^{\text{I}}$ distance compares with that observed for the other complexes **2**, **3** and **6** (Table 4), indicating no constraint within the six-membered ring formed upon the $1\kappa\text{N}:2\kappa\text{P}$ coordination of the incoming ligand **1**. The $\text{Cu}\text{-N}$ bond lengths of the $\text{Cu}_2(\mu\text{-}1\kappa\text{N}:1,2\kappa\text{P}:2\kappa\text{N}\text{-phosphole})$ core are almost identical and similar to those observed for complexes **2**, **3** and **6** (Table 4). Likewise, the $\text{N}\text{-Cu}\text{-}\mu\text{-P}$ and $\text{Cu}\text{-}\mu\text{-P}\text{-Cu}$ angles are unremarkable (Table 4). The only structural parameters influenced by the local dissymmetry of the complex are the $\mu\text{-P}\text{-Cu}$ distances. They are markedly different (Table 4, $\Delta(\mu\text{-P}\text{-Cu})=0.087\text{ \AA}$), the shortest $\text{P}\text{-Cu}$ distance being observed for Cu2, which has a nitrogen-rich environment. These structural data confirm that a phosphane donor can easily move from a symmetrical to a unsymmetrical bridging position and that there is a continuum between these two coordination modes.

The synthesis of complexes **6** (Scheme 2) **7** and **8** (Scheme 3) showed that ligand exchange reactions can be easily performed with a range of ligands that have very different properties (N,N/P-P/P-P-N donors; 1,3/1,4-chelates) without decoordination of the $\mu\text{-}1\kappa\text{N}:1,2\kappa\text{P}:2\kappa\text{N}$ donor **1**, which features a bridging P centre. These results prompted us to further investigate this type of reaction using dimers **7** and **8** (Scheme 3), which still possess two labile acetonitrile ligands.

Ligand exchange on dimers **7** and **8** involving dppm and phosphole **1**:

Complex **7** reacted with one equivalent of dppm affording dimer **9** (Scheme 3), isolated as an air-stable yellow powder in 86% yield. Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a well-defined triplet-of-triplets centred at $\delta=10.7\text{ ppm}$ ($J(\text{P,P})=31.4\text{ Hz}$ and 62.3 Hz), two broad signals centred at $\delta=-2.7$ and -7.0 ppm and the PF_6^- signals ($\delta=-144.3\text{ ppm}$, $J(\text{P,F})=710.0\text{ Hz}$). The most deshielded signal can be assigned to the bridging phosphole by analogy with the data of previously synthesised Cu^{I} dimers (Table 1), with its multiplicity being due to the fact that the two dppm ligands are not magnetically equivalent (Scheme 3). The integration of the ^1H NMR spectrum confirmed that **9** contains one bis(2-pyridyl)phosphole **1** and two dppm ligands; no signals assignable to coordinated acetonitrile ligands were ob-

served. The proposed structure for dimer **9** was confirmed by a single-crystal X-ray diffraction study. A solution of **9** in CH_2Cl_2 was exposed to pentane vapours for one week under air, resulting in the formation of crystals with three different morphologies in approximately equivalent amounts: pale yellow prisms (**9a**; monoclinic space group $P2_1/n$), pale yellow needles (**9b**; triclinic space group $P\bar{1}$) and pale yellow needles (**9c**; monoclinic space group $P2_1/n$; Table 3). The asymmetric unit of **9a** contains one dicationic bimetallic complex **9**, two hexafluorophosphate counterions, two CH_2Cl_2 molecules and one molecule of water. The asymmetric unit of **9b** contains two independent dicationic dimers **9**, four hexafluorophosphate counterions and one CH_2Cl_2 molecule. As observed for complexes **7a** and **b**, the dicationic complexes **9a** and **9b** are conformers that simply differ by the mutual disposition (**9a**, *cisoid*; **9b**, *transoid*) of the methylene moiety of one dppm ligand with respect to the μ -P centres (Figure 8). It is worth noting that the $\text{Cu}^1\text{-Cu}^1$ dis-

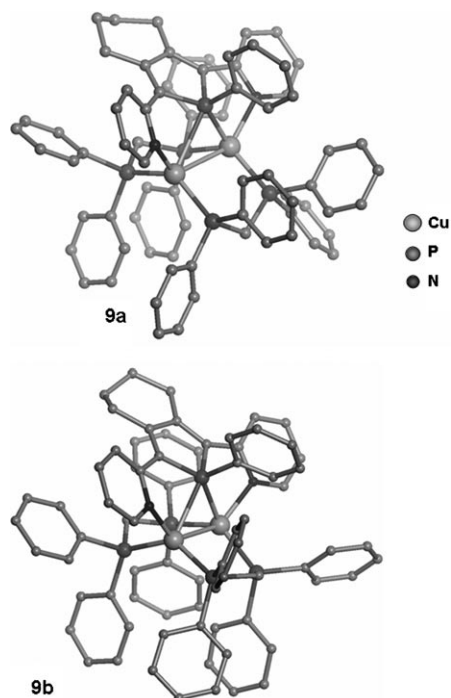


Figure 8. Molecular structure of dicationic complexes **9a** and **9b**. Hydrogen atoms have been omitted for clarity.

tances (**9a**: 2.8329(9) Å; **9b**: 2.8743(6) and 2.9501(6) Å) are notably longer than those observed for the related dimers (Table 4). Although complexes **9a,b** are highly symmetric, the two μ -P atoms do not exhibit a symmetrically bridging coordination mode (Table 4). Remarkably, the tiny structural difference between dimers **9a** and **9b** (*cisoid* and *transoid* arrangement of one dppm toward the μ -P centres) has an impact on the coordination geometry of the bridging P centre, since the P–Cu distances are different for the two conformers ($\Delta(\mu\text{-P-Cu})$: **9a**, 0.13 Å; **9b**, 0.04 and 0.06 Å).

The asymmetric unit of crystals **9c** contains three independent *transoid* conformers that have $\text{Cu}_2(\mu\text{-P})$ cores in which the $\Delta(\mu\text{-P-Cu})$ increases from 0.07 to 0.47 Å. Once again, this variation observed within one cell of a complex, with a highly symmetric gross structure, highlights that there is a continuum between symmetrically and semibridging coordination modes for phosphanes. The switch from bridging to semibridging coordination mode requires a minimum of energy and can be induced by weak (steric, π - π , $\text{CH}-\pi$, etc.) interactions. Conformers **9c** reveal another interesting feature. The $\text{Cu}^1\text{-Cu}^1$ distances are long (2.85–2.95 Å, Table 4) ruling out cuprophilic interactions.^[14] Hence, for the first time, it is shown that the P centre of the phosphole ring can adopt a bridging coordination mode in dimers that do not display metal–metal interactions. This result is a further step towards the establishment of phosphanes as routine bridging ligands.

The last ligand exchange reaction that was investigated involved dimer **8** and ligand **1** (Scheme 3). This led to the isolation of complex **10**^[6d] as an air-stable red powder in 81% yield. In addition to the resonances due to the PF_6^- ion, its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 exhibits two broad singlets at $\delta = 12.0$ ($\nu_{1/2} = 103$ Hz) and 4.9 ppm ($\nu_{1/2} = 290$ Hz). As observed for its precursor, that is, complex **8**, the broadness of these ^{31}P NMR signals suggests fluxional behaviour. The fact that only one set of signals assignable to the three coordinated ligands **1** was observed in the ^1H NMR and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra confirms this hypothesis. Single crystals were collected after a solution of **10** in THF was exposed to pentane and these were subjected to an X-ray diffraction study (Tables 3 and 4) revealing that **10** is a Cu^1 dimer featuring three ligands: one molecule of **1** acting as a 6-electron μ -1 κN :1,2 κP :2 κN donor and two molecules of **1** acting as 1 κN :2 κP chelates (Figure 9). The two Cu^1 centres possess either a phosphorus- or nitrogen-rich coordination sphere. Not surprisingly, in such a dissymmetric environment, the coordination mode of the μ -P centre is semibridging ($\Delta(\mu\text{-P-Cu})$: 0.295 Å). It is notable that, as observed in complex **8**, the shortest P–Cu distance observed is that for

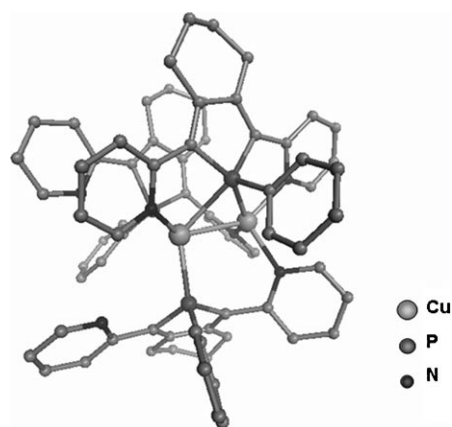


Figure 9. Molecular structure of dicationic complex **10**. Hydrogen atoms have been omitted for clarity.

which the Cu centre has a nitrogen-rich coordination sphere. The other metric parameters of the N,P,N pincer compare with those of complex **8** (Table 5).

Stability of Cu^I dimers assembled by the N,P,N pincer **1**:

Complexes **2**, **3** and **6–10** are solids that can be stored indefinitely under air at room temperature. They are stable in CH₂Cl₂ or THF under air for several weeks. Derivative **1** is thus a very efficient ligand for stabilizing Cu^I dimers, which are potentially prone to oxidation. This is nicely illustrated by the fact that decomposition of complex **7**, bearing labile acetonitrile ligands, in nondistilled THF solution was observed only upon heating at 60 °C for one month in air (Scheme 4). In the ³¹P{¹H} spectrum of the crude solution, apart from the signals of **7** (Table 1), a triplet centred at δ = −9.25 ppm with a large *J*(P,F) coupling constant (975.7 Hz) was observed, indicating the presence of a PF₂ fragment. This solution was exposed to pentane vapour affording a large quantity of yellow crystals of **7** along with few tiny orange crystals, which were submitted to an X-ray diffraction study (Table 3). The asymmetric unit of these orange crystals contains one monocationic complex **11** (Scheme 4, Figure 10), one disordered hexafluorophosphate counterion

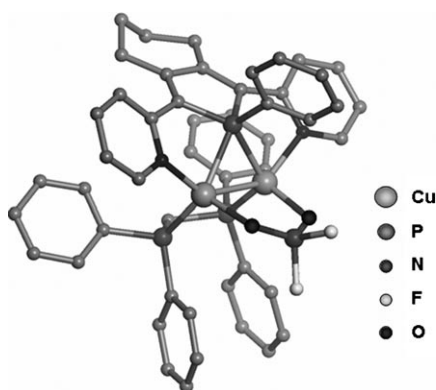
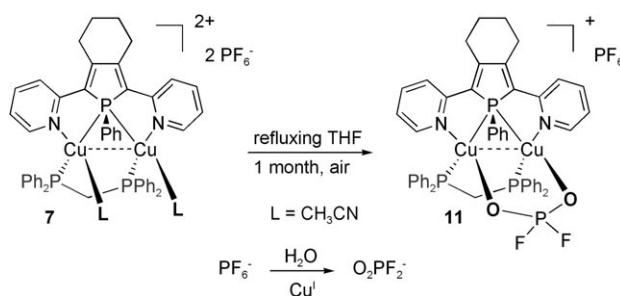


Figure 10. Molecular structure of cationic complex **11**. Hydrogen atoms have been omitted for clarity.

and five disordered CH₂Cl₂ solvent molecules. Derivative **11** still features a μ-1κN:1,2κP:2κN ligand **1** with a semibringing P centre (Table 4) and a 1κP:2κP-dppm ligand. The Cu^I coordination spheres are completed by a PF₂O₂[−] fragment. Note that the metric data of complex **11** compare well with those of its precursor **7** (Tables 4 and 5). The PF₂O₂[−] fragment arises from hydrolysis of hexafluorophosphate anions, a process that is known to be catalysed by Lewis acids (Scheme 5).^[15] It is likely that the Cu^I centres of **7**, which each bear a labile acetonitrile ligand, can act both as Lewis acids and as fluorine scavengers favouring the PF₆[−] → PF₂O₂[−] transformation. However, this transformation occurs very slowly (1 month) under rather drastic conditions (refluxing crude THF at air) and in low yield (<5%), confirming the intrinsically high stability of Cu^I dimers assembled



Scheme 5. Hydrolysis of complex **7**.

by bis(2-pyridyl)phosphole **1** bearing a bridging phosphane centre.

Conclusion

In this paper, we have described the synthesis, structural characterisation and reactivity of a novel series of metal dimers assembled by an N,P,N pincer featuring a bridging P centre. This study has revealed that bridging phosphane-based ligands are able to stabilise bimetallic species featuring metals with diverse electron counts and coordination geometries. Another important result is that there is a continuum between bridging and semibringing coordination modes for μ-phosphanes, as is already well established for CO, which is the prototypical bridging ligand. The ease with which the μ-P centre of the phosphole ring adopts a bridging geometry is probably due to the fact that the P lone pair has a high s character and thus is not directional. Finally, reactions familiar from classical coordination chemistry, such as ligand exchanges, can be performed with a wide range of donors on dimers featuring bridging phosphane centres.^[16] These results show that chelates featuring bridging phosphanes are versatile binucleating ligands and that phosphanes now have to be considered as classical bridging ligands. We believe that these results should encourage the design of novel assembling ligands based on bridging phosphane donors.

Experimental Section

Details of the X-ray crystallography studies: Single crystals suitable for X-ray crystal analysis were obtained at room temperature by slow diffusion of pentane vapour into solutions of complexes **2**, **3** and **5–9** in dichloromethane and by slow diffusion of pentane vapour into solutions of complexes **10** and **11** in THF. Single-crystal data collection was performed at 120 K with a Nonius KappaCCD diffractometer or at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with MoK_α radiation (λ = 0.71069 Å). Reflections were indexed, Lorentz-polarisation corrected and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed by using the SCALEPACK program.^[17] Structure determinations were performed by direct methods with the solving program SIR97,^[18] that revealed all the non-hydrogen atoms. The SHELXL program^[19] was used to refine the structures by full-matrix least-squares

methods 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 studied, with the exception of complex **2**, dichloromethane or THF solvent molecules were found in addition to the cationic coordination complexes and to their counterions (hexafluorophosphate). In some cases, these solvent molecules were found to be highly disordered, leading to rather high anisotropic displacement parameters for some of these atoms. As a consequence, final agreement (R) factors were determined with modest values in some cases (Tables 2 and 3). Nevertheless, anisotropic displacement parameters associated with the atoms of the cationic coordination complexes are always satisfactory. This allows a primary assignment of these modest $R1$ and $wR2$ factors of the complexes **5**, **9** and **10** to an inadequate modelling of the counterions and the solvent molecules present in the unit cell and lends confidence to the treatment of the structural resolution of these derivatives. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.^[20] CCDC 262842 (**2**), 656994 (**3**), 656995 (**5**), 656996 (**6**), 293233 (**7a**), 656997 (**7b**), 262843 (**8**), 656998 (**9a**), 656999 (**9b**), 657000 (**9c**), 262844 (**10**) and 657001 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

General information: All experiments were performed under an atmosphere of dry argon by using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (diethyl ether, THF) or from phosphorus pentoxide (dichloromethane, acetonitrile). ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker AV300, DPX200 or AV500 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 . Assignment of carbon atoms was based on HMBC and HMQC experiments. Elemental analyses were performed by the CRMPO, University of Rennes 1. 1-Phenyl-2,5-bis(2-pyridyl)phosphole (**1**) was synthesised as previously reported.^[8]

[Cu₂(CH₃CN)₄{1-phenyl-2,5-bis(2-pyridyl)phosphole}]₂(PF₆)₂ (2**):** [Cu(CH₃CN)₄]₂PF₆ (0.405 g, 1.10 mmol, 2 equiv) was added to a solution of **1** (0.200 g, 0.55 mmol) in THF (10 mL) at RT. The mixture was stirred for 10 h at RT and a yellow precipitate was formed. The volatile materials were removed under vacuum and the product was isolated as a yellow powder (0.490 g, 95%). Yellow crystals suitable for X-ray diffraction study were obtained at RT by slow diffusion of pentane into a solution of **2** in CH₂Cl₂. ^1H NMR (300 MHz, CD₂Cl₂): δ = 1.87–2.01 (m, 4H; C=CCH₂CH₂), 2.3 (s, 12H; CH₃CN), 2.93 (m, 2H; C=CCH₂), 3.19 (m, 2H; C=CCH₂), 7.30 (brt, J = 7.2 Hz, 2H; *m*-Ph), 7.35–7.50 (m, 5H; H⁵ Py, *o*,*p*-Ph), 7.83 (brd, J = 8.0 Hz, 2H; H³ Py), 8.02 (brt, J = 7.8 Hz, 2H; H⁴ Py), 8.63 ppm (brs, 2H; H⁶ Py); ^{13}C NMR (75.46 MHz, CD₂Cl₂): δ = 2.2 (s; CH₃CN), 21.7 (s; C=CCH₂CH₂), 28.0 (s; C=CCH₂), 118.3 (s; CH₃CN), 123.8 (s; C⁵ Py), 124.5 (s; C³ Py), 129.6 (d, J (P,C) = 9.9 Hz; *m*-Ph), 132.1 (s; *p*-Ph), 132.7 (d, J (P,C) = 13.2 Hz; *o*-Ph), 139.5 (s; C⁴ Py), 150.3 (s; C⁶ Py), 150.9 (m; C⁶), 152.1 ppm (s; C² Py). C⁶ and *ipso*-Ph not observed; ^{31}P NMR (121.5 MHz, CD₂Cl₂): δ = -144.3 (sept, 1J (P,F) = 709.5 Hz; PF₆); -0.1 ppm ($\nu_{1/2}$ = 85 Hz); elemental analysis calcd (%) for C₃₂H₃₃N₆P₃F₁₂Cu₂ (949.64): C 40.47, H 3.50, N 8.85; found: C 40.61, H 3.63, N 8.71.

[Cu₂Cl₂{1-phenyl-2,5-bis(2-pyridyl)phosphole}]₂ (3**):** CuCl (0.108 g, 1.10 mmol, 2 equiv) was added to a solution of **1** (0.200 g, 0.55 mmol) in CH₂Cl₂ (10 mL) at RT. The mixture was stirred for 3 h at RT and the solution turned deep red. The volatile materials were removed under vacuum, the solid was washed with Et₂O (2 × 10 mL) and the product was isolated as a red powder (0.235 g, 76%). ^1H NMR (300 MHz, CD₂Cl₂): δ = 1.57–1.71 (m, 8H; C=CCH₂CH₂), 1.85–1.97 (m, 4H; C=CCH₂), 2.95–3.21 (m, 4H; C=CCH₂), 7.25 (brt, J = 7.5 Hz, 8H; H⁵ Py, *m*-Ph), 7.72 (m, 4H; H³ Py), 7.83 (brm, 6H; *o*,*p*-Ph), 7.91 (brt, J = 7.5 Hz, 4H; H⁴ Py), 8.84 ppm (brs, 4H; H⁶ Py); ^{31}P NMR (121.5 MHz, CD₂Cl₂): δ =

0.1 ppm ($\nu_{1/2}$ = 220 Hz); elemental analysis calcd (%) for C₄₈H₄₂Cl₄Cu₂N₄P₂ (1132.82): C 50.89, H 3.74, N 4.95; found: C 50.64, H 3.50, N 4.65.

[Cu{1-phenyl-2-(2-pyridyl)-5-(2-thienyl)phosphole}]₂(PF₆)₂ (5**):** [Cu(CH₃CN)₄]₂PF₆ (0.020 g, 0.05 mmol, 0.5 equiv) was added to a solution of **4** (0.040 g, 0.1 mmol) in CH₂Cl₂ (10 mL) at RT. The mixture was stirred for 2 h at RT and the solution turned deep red. The volatile materials were removed under vacuum, the solid was washed with Et₂O (2 × 10 mL) and the product was isolated as a red powder (0.025 g, 54%). ^1H NMR (200 MHz, CDCl₃): δ = 1.75–2.10 (m, 8H; C=CCH₂CH₂), 2.50–3.10 (m, 8H; C=CCH₂), 6.80–7.00 (brm, 8H; H⁵ Py, H⁴ thio, *m*-Ph), 7.00–7.40 (brm, 10H; H³ thio, H⁵ thio and *o*,*p*-Ph), 7.65 (m, 2H; H⁴ Py), 7.85 (m, 2H; H³ Py), 7.90–8.25 ppm (brs, 2H; H⁶ Py); ^{31}P NMR (121.5 MHz, CD₂Cl₂): δ = +14.0 ppm ($\nu_{1/2}$ = 202 Hz).

[Cu₂(2,2'-bipyridine)₂{1-phenyl-2,5-bis(2-pyridyl)phosphole}]₂(PF₆)₂ (6**):** 2,2'-Bipyridine (0.033 g, 0.22 mmol) was added to a solution of complex **2** (0.100 g, 0.11 mmol) in CH₂Cl₂ (10 mL) at RT. The yellow solution immediately became red-orange. The mixture was stirred for 30 min at RT and the volatile materials were removed under vacuum. The solid was washed with Et₂O (2 × 10 mL) and the product was isolated as an orange powder (0.0523 g, 70%). ^1H NMR (300 MHz, CD₂Cl₂): δ = 2.07–2.13 (m, 4H; C=CCH₂CH₂), 3.27 (m, 4H; C=CCH₂), 7.19 (t, J = 7.3 Hz, 2H; *m*-Ph), 7.29–7.33 (brs, 4H; *o*-Ph, H⁵ Py), 7.49 (brs, 4H; H⁵ bipy), 7.57 (brt, J = 7.3 Hz, 1H; *p*-Ph), 7.75 (brs, 2H; H³ Py), 7.76 (brs, 2H; H⁴ Py), 7.91 (m, 12H; H³ bipy, H⁴ bipy, H⁶ bipy), 8.08 ppm (brs, 2H; H⁶ Py); ^{13}C NMR (75.46 MHz, CD₂Cl₂): δ = 22.3 (s; C=CCH₂CH₂), 28.7 (d, J (P,C) = 6.7 Hz; C=CCH₂), 122.4 (brs; C_{arom}), 123.9 (s; C_{arom}), 124.9 (d, J (P,C) = 4.5 Hz; C_{arom}), 127.0 (s; C_{arom}), 130.5 (d, J (P,C) = 10.7 Hz; *p*-Ph), 131.4 (d, J (P,C) = 14.0 Hz; *m*-Ph), 132.1 (brs; *o*-Ph), 139.6 (brs; C_{arom}), 140.0 (brs; C_{arom}), 149.7 (s; C⁶ Py), 149.9 (brs; C⁶ Py), 151.9 ppm (m, C² Py; C⁵ Py); ^{31}P NMR (121.5 MHz, CD₂Cl₂): δ = -144.3 (sept, 1J (P,F) = 709.5 Hz; PF₆), +3.0 ppm (brs; 1P); elemental analysis calcd (%) for C₃₃H₃₃N₆P₃F₁₂Cu₂ (1140.15): C 49.44, H 3.99, N 7.36; found: C 49.57, H 3.83, N 7.21.

[Cu₂(CH₃CN)₂(dppm){1-phenyl-2,5-bis(2-pyridyl)phosphole}]₂(PF₆)₂ (7**):** 1,1'-Bis(diphenylphosphino)methane (0.162 g, 0.42 mmol, 1 equiv) was added to a solution of complex **2** (0.400 g, 0.42 mmol) in CH₂Cl₂ (15 mL) at RT. The yellow mixture was stirred for 30 min at RT and the volatile materials were removed under vacuum. The solid was washed with Et₂O (2 × 10 mL) and **7** was obtained after precipitation from CH₂Cl₂/diethyl ether as an air-stable yellow solid (0.478 g, 91% yield). ^1H NMR (300 MHz, CD₂Cl₂): δ = 1.68–1.80 (m, 2H; C=CCH₂CH₂), 2.00–2.10 (m, 2H; C=CCH₂CH₂), 2.25 (s, 6H; H_{CH₃CN}), 2.64 (m, 2H; C=CCH₂), 2.88 (dt, 2J (H,H) = 14.1 Hz, 2J (P,H) = 10.1 Hz, 1H; CH_{2dppm}), 3.20 (m, 2H; C=CCH₂), 3.42 (dt, 2J (H,H) = 14.1 Hz, 2J (P,H) = 10.1 Hz, 1H; CH_{2dppm}), 6.80 (dd, 3J (H,H) = 7.5, 7.5 Hz, 4H; *m*-Ph_{dppm}), 7.04 (dd, 3J (H,H) = 7.5, 7.5 Hz, 4H; *m*-Ph_{dppm}), 7.32 (dd, 3J (H,H) = 5.1, 7.6 Hz, 2H; H⁵ Py), 7.35–7.48 (m, 17H; *o*-Ph_{dppm}, *p*-Ph_{dppm}, *o*,*p*,*m*-Ph), 7.79 (d, 3J (H,H) = 8.0 Hz, 2H; H³ Py), 7.94 (dd, 3J (H,H) = 7.6, 8.0 Hz, 2H; H⁴ Py), 8.31 ppm (d, 3J (H,H) = 5.1 Hz, 2H; H⁶ Py); ^{13}C NMR (75.46 MHz, CD₂Cl₂): δ = 2.0 (brs; CH₃CN), 21.9 (s; C=CCH₂CH₂), 23.5 (brs; CH_{2dppm}), 28.0 (d, J (P,C) = 6.1 Hz; C=CCH₂), 117.3 (s; CH₃CN), 123.7 (s; C⁵ Py), 124.5 (d, J (P,C) = 5.1 Hz; C³ Py), 128.9 (d, J (P,C) = 4.7 Hz; C_{ph}), 129.0 (d, J (P,C) = 5.0 Hz; C_{ph}), 129.5 (d, J (P,C) = 10.8 Hz; C_{ph}), 130.7 (s; C_{ph}), 131.0 (s; C_{ph}), 131.4 (d, J (P,C) = 7.2 Hz; C_{ph}), 131.6 (d, J (P,C) = 7.2 Hz; C_{ph}), 131.9 (d, J (P,C) = 3.5 Hz; C_{ph}), 132.1 (d, J (P,C) = 5.9 Hz; C_{ph}), 132.3 (d, J (P,C) = 5.9 Hz; C_{ph}), 139.0 (s; C⁴ Py), 150.0 (brs; C⁶ Py), 152.9 (brs; C² Py), 153.8 ppm (brs; C⁶), C⁴ and *ipso*-Ph not observed; ^{31}P NMR (CD₂Cl₂, 121.5 MHz): δ = -144.3 (sept, 1J (P,F) = 709.5 Hz; PF₆), -1.6 (d, 2J (P,P) = 82.6 Hz; P_{dppm}), +13.7 ppm (t, 2J (P,P) = 82.6 Hz; P_{phosphole}); elemental analysis calcd (%) for C₅₃H₄₉Cu₂F₁₂N₄P₅ (1251.93): C 50.85, H 3.95, N 4.48; found: C 50.91, H 3.85, N 4.55.

[Cu₂(CH₃CN)₂{1-phenyl-2,5-bis(2-pyridyl)phosphole}]₂(PF₆)₂ (8**):** One equivalent of **1** (0.096 g, 0.26 mmol) was added to a solution of complex **2** (0.250 g, 0.26 mmol) in CH₂Cl₂ (15 mL) at room temperature. This mixture was stirred for 3 h at room temperature and the volatile materials were removed under vacuum. The solid was washed with Et₂O (2 × 10 mL) and **8** was obtained after precipitation from CH₂Cl₂/diethyl ether

as an air-stable orange solid (0.277 g, 85% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.80–1.94 (m, 8H; $\text{C}=\text{CCH}_2\text{CH}_2$), 2.00 (s, 6H; CH_3CN), 2.22–2.62 (m, 4H; $\text{C}=\text{CCH}_2$), 2.89–3.00 (m, 4H; $\text{C}=\text{CCH}_2$), 7.29 (brs, 4H; *m*-Ph), 7.32–7.51 (m, 10H; H^5 Py, *o,p* Ph), 7.85–8.05 (m, 8H; H^3 Py, H^4 Py), 8.43 ppm (brs, 4H; H^6 Py); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CD_2Cl_2): δ = 3.8 (brs; CH_3CN), 23.9 (s; $\text{C}=\text{CCH}_2\text{CH}_2$), 30.1 (brs; $\text{C}=\text{CCH}_2$), 120.7 (brs; CH_3CN), 125.5 (brs; C^5 Py), 126.4 (s; C^3 Py), 131.4 (brs; *m*-Ph), 133.6 (brs; *p*-Ph), 134.4 (brs; *o*-Ph), 140.8 (brs; C^4 Py), 151.9 (brs; C^6 Py), 152.9 (brs; C^2 Py), 153.8 ppm (brs; C^6), C^a and *ipso*-Ph not observed; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): δ = -144.3 (sept, $^1J(\text{P,F})$ = 709.5 Hz; PF_6), +8.9 ppm (brs, $\nu_{1/2}$ = 117 Hz); elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{48}\text{N}_6\text{P}_4\text{F}_{12}\text{Cu}_2$ (1235.95) : C 50.53, H 3.91, N 6.80; found: C 50.34, H 3.79, N 6.91.

[Cu₂(dppm)₂(1-phenyl-2,5-bis(2-pyridyl)phosphole)](PF₆)₂ (9): 1,1'-Bis(diphenylphosphino)methane (0.161 g, 0.42 mmol, 1 equiv) was added to a solution of complex **7** (0.400 g, 0.42 mmol) in CH_2Cl_2 (15 mL) at RT. The yellow mixture was stirred for 3 h at RT and the volatile materials were removed under vacuum. The solid was washed with pentane (2×10 mL) and **9** was obtained after precipitation from CH_2Cl_2 /diethyl ether as an air-stable yellow solid (0.560 g, 86% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.90–1.98 (m, 2H; $\text{C}=\text{CCH}_2\text{CH}_2$), 2.00–2.10 (m, 2H; $\text{C}=\text{CCH}_2\text{CH}_2$), 2.33–2.42 (m, 2H; $\text{C}=\text{CCH}_2$), 2.47 (dt, $^2J(\text{H,H})$ = 15.00 Hz, $^2J(\text{P,H})$ = 9.12 Hz, 1H; $\text{CH}_{2\text{dppm}}$), 2.94–3.17 (m, 2H; $\text{C}=\text{CCH}_2$), 3.43–3.62 (brm, 2H; $\text{CH}_{2\text{dppm}}$, $\text{CH}'_{2\text{dppm}}$), 3.73 (dt, $^2J(\text{H,H})$ = 9.50 Hz, $^2J(\text{P,H})$ = 9.47 Hz, 1H; $\text{CH}'_{2\text{dppm}}$), 6.88–6.97 (brm, 8H; H Ph_{dppm}), 7.01–7.12 (brm, 16H; H Ph_{dppm}), 7.15–7.30 (brm, 18H; H^5 Py, H Ph_{dppm}), 7.41–7.55 (m, 7H; H^3 Py, (*o,p,m*-)Ph), 7.76 (t, $^3J(\text{H,H})$ = 7.6 Hz, 2H; H^4 Py), 8.12 ppm (d, $^3J(\text{H,H})$ = 4.86 Hz, 2H; H^6 Py); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CD_2Cl_2): δ = 21.7 (s; $\text{C}=\text{CCH}_2\text{CH}_2$), 28.1 (d, $J(\text{P,C})$ = 5.6 Hz; $\text{C}=\text{CCH}_2$), 124.2 (s; C^5 Py), 124.9 (d, $^3J(\text{P,C})$ = 4.8 Hz; C^3 Py), 128.6 (d, $J(\text{P,C})$ = 5.1 Hz; C_{ph}), 128.8 (d, $J(\text{P,C})$ = 5.1 Hz; C_{ph}), 129.1 (d, $J(\text{P,C})$ = 4.6 Hz; C_{ph}), 129.3 (d, $J(\text{P,C})$ = 4.6 Hz; C_{ph}), 129.5 (brm; C_{ph}), 129.7 (s; C_{ph}), 129.9 (d, $J(\text{P,C})$ = 9.9 Hz; C_{ph}), 130.4 (s; C_{ph}), 131.3 (brm; C_{ph}), 131.9 (brm; C_{ph}), 132.7 (d, $J(\text{P,C})$ = 7.5 Hz; C_{ph}), 132.9 (d, $J(\text{P,C})$ = 7.5 Hz; C_{ph}), 133.4 (t, $J(\text{P,C})$ = 7.5 Hz; C_{ph}), 139.4 (s; C^4 Py), 150.5 (brs; C^6 Py), 152.2 (d, $J(\text{P,C})$ = 7.5 Hz; C^2 Py), 152.6 ppm (brs; C^6), $\text{CH}_{2\text{dppm}}$, C^a and *ipso*-Ph not observed; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.5 MHz): δ = -144.3 (sept, $^1J(\text{P,F})$ = 709.5 Hz; PF_6), -7.0 (t, $^2J(\text{P,P})$ = 67.4 Hz; P_{dppm}), -2.7 (brm; P_{dppm}), +10.7 ppm (sept, $^2J(\text{P,P})$ = 38.6, 19.5 Hz; $\text{P}_{\text{phosphole}}$); elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{68}\text{Cu}_2\text{F}_{12}\text{N}_8\text{P}_7$ (1552.19): C 57.19, H 4.22, N 1.80; found: C 57.31, H 4.01, N 1.64.

[Cu₂{1-phenyl-2,5-bis(2-pyridyl)phosphole}₃][PF₆]₂ (10): Ligand **1** (0.059 g, 0.16 mmol, 1 equiv) was added to a solution of complex **8** (0.200 g, 0.16 mmol) in CH_2Cl_2 (15 mL) at RT. The mixture was stirred for 3 h at RT and the volatile materials were removed under vacuum. The solid was washed with diethyl ether (2×10 mL) and **10** was obtained after precipitation from CH_2Cl_2 /diethyl ether as an air-stable red solid (0.199 g, 81% yield). ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.52–1.7 (m, 6H; $\text{C}=\text{CCH}_2\text{CH}_2$), 1.83–1.90 (m, 6H; $\text{C}=\text{CCH}_2\text{CH}_2$), 2.10–2.59 (m, 6H; $\text{C}=\text{CCH}_2$), 2.85–3.07 (m, 6H; $\text{C}=\text{CCH}_2$), 6.46 (t, $J(\text{H,H})$ = 8.2 Hz, 1H; *m*-Ph), 6.72 (t, $J(\text{H,H})$ = 6.5 Hz, 1H; *m*-Ph), 6.91 (t, $J(\text{H,H})$ = 7.1 Hz, 1H; *m*-Ph), 6.95–7.07 (m; H^4 Py), 7.05–7.18 (m; 5H_{arom}), 7.21 (t, $J(\text{H,H})$ = 6.7 Hz; 1H_{arom}), 7.20–7.40 (m; 8H_{arom}), 7.55–7.80 (m; H^6 Py, 1H), 7.84 (t, $J(\text{H,H})$ = 7.6 Hz; 1H_{arom}), 7.90 (t, $J(\text{H,H})$ = 7.3 Hz; 1H_{arom}), 8.05–8.15 (m, H^4 Py; 1H), 8.20–8.60 ppm (brs, H^6 Py; 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD_2Cl_2): δ = 21.9 (s; $\text{C}=\text{CCH}_2\text{CH}_2$), 22.1 (s; $\text{C}=\text{CCH}_2\text{CH}_2$), 28.4 (brs; $\text{C}=\text{CCH}_2$), 125.5 (brs; C^5 Py), 123.4 (brs; C^3 Py), 123.6 (brs; C^3 Py), 128.7 (brs; *m*-Ph), 128.9 (brs; *m*-Ph), 130.1 (brs; *m*-Ph), 130.9 (brs; *o,m*-Ph), 131.6 (brs; *o,p*-Ph), 132.1 (brs; *o,p*-Ph), 133.1 (brs; *o,p*-Ph), 137.9 (brs; C^4 Py), 138.8 (s; C^4 Py), 139.6 (s; C^4 Py), 149.4 (s; C^4 Py), 149.8 (brs; C^6 Py), 150.2 ppm (brs; C^6 Py), C^a , C^b and *ipso*-Ph not found; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.4 MHz, CD_2Cl_2): δ = -144.3 (sept, $^1J(\text{P,F})$ = 709.5 Hz; PF_6), +4.9 (brs, $\nu_{1/2}$ = 290 Hz), +12.0 ppm (brs; $\nu_{1/2}$ = 103 Hz); elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{63}\text{N}_6\text{P}_5\text{F}_{12}\text{Cu}_2$ (1522.25) : C 56.81, H 4.17, N 5.52; found: C 56.97, H 4.23, N 5.40.

[Cu₂(dppm){1-phenyl-2,5-bis(2-pyridyl)phosphole}(PO₂F₂)PF₆ (11): A solution of complex **7** (0.5 g, 0.4 mmol) in THF (18 mL) was heated at 60°C for 4 weeks. The solution was exposed to pentane vapour diffusion

and a small amount complex **11** was formed as deep orange crystals along with a large amount of crystalline complex **7** (forms **7a** and **7b**). Careful hand separation of these crystals allowed a pure sample of complex **11** to be obtained for spectroscopic characterisation. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.68–1.80 (m, 2H; $\text{C}=\text{CCH}_2\text{CH}_2$), 1.92–2.10 (m, 2H; $\text{C}=\text{CCH}_2\text{CH}_2$), 2.73 (brm, 2H; $\text{C}=\text{CCH}_2$), 2.87 (dt, $^2J(\text{H,H})$ = 13.37 Hz, $^2J(\text{P,H})$ = 10.08 Hz; 1H, $\text{CH}_{2\text{dppm}}$), 3.10 (brm, 3H; $\text{CH}_{2\text{dppm}}$, $\text{C}=\text{CCH}_2$), 7.06–7.41 (m, 27H, H Ph_{dppm}; H Ph, H^5 Py), 7.71 (d, $^3J(\text{H,H})$ = 7.46 Hz, 2H; H^3 Py), 7.83 (t, $^3J(\text{H,H})$ = 7.6 Hz; 2H, H^4 Py), 8.20 ppm (s, 2H; H^6 Py); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CD_2Cl_2): δ = 22.3 (s; $\text{C}=\text{CCH}_2\text{CH}_2$), 28.2 (d, $J(\text{P,C})$ = 6.0 Hz; $\text{C}=\text{CCH}_2$), 123.7 (s; C^5 Py), 129.4 (s; C^3 Py), 129.5–129.8 (m; C_{ph}), 131.3 (d; $J(\text{P,C})$ = 17.3 Hz, C_{ph}), 133.1 (m; C_{ph}), 139.3 (s; C^4 Py), 151.2 (s; C^6 Py), 152.9 ppm (brs; C^2 Py), C^b , C^c , $\text{CH}_{2\text{dppm}}$ and *ipso*-Ph not observed; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.5 MHz): δ = -144.4 (sept, $^1J(\text{P,F})$ = 710.7 Hz; PF_6), -9.25 (t, $^1J(\text{P,F})$ = 974.7 Hz; PO_2F_2), -2.1 (brm; P_{dppm}), +14.9 ppm (brm; $\text{P}_{\text{phosphole}}$).

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