Coordination Modes

Bridging Phosphanes: Exotic or Versatile Binucleating Ligands?**

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The recent discovery that tertiary phosphanes PR_3 can act as bridging ligands[1] (**A**, Figure 1) was a breakthrough in coordination chemistry,[2] since binucleating ligands potentially allow the synthesis of di- and polynuclear complexes that are of great interest in many fields, such as catalysis, bioinorganic chemistry, and materials sciences.[3] Up to now, only two types of binuclear compounds bearing symmetrically bridging phosphanes are known (Rh^{I}[1] (**C**) and Pd^{I}[4] homodimers (**D**), Figure 1). In order to establish phosphanes as versatile binucleating ligands, it is necessary to show that they can effectively stabilize other dinuclear fragments, and that they possess properties typical of well-established bridging ligands.[3] In this paper we describe the synthesis and characterization in the solid state of the first heterobimetallic complex and the first copper(I) homodimers bearing bridging phosphane ligands. Furthermore, we show that there is a continuum between symmetrically bridging (**A**) and semi-bridging (**B**)[5] coordination modes (Figure 1), a key structural feature analogous to that observed for CO,[6] which is the archetypal bridging ligand.

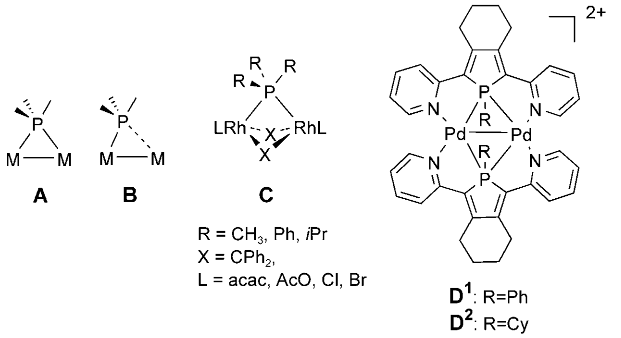
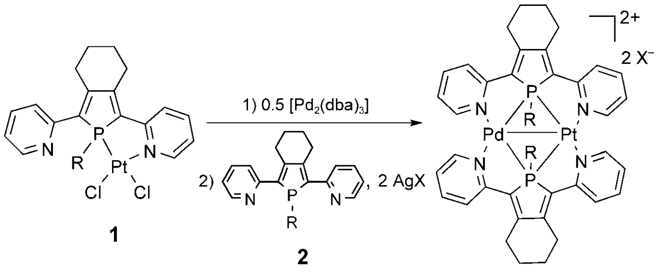


Figure 1. Bridging (**A**) and semi-bridging (**B**) coordination modes for phosphanes, and complexes **C** and **D** bearing bridging phosphanes. acac = acetylacetonate; Cy = cyclohexyl.

We have synthesized a heteronuclear Pd–Pt analog of complex **D^1** (Figure 1) by a stepwise method, which allows the sequential introduction of the metal centers.[4b] Treatment of Pt^{II} complex **1** with Pd^0, 2,5-bis(2-pyridyl)phosphole (**2**),[7] and two equivalents of AgOTf gave derivative **3**, which was isolated as an air-stable red powder (69% yield, Scheme 1).



Scheme 1. Synthesis of Pd^{I}–Pt^{I} heterodimer **3**.

High-resolution mass spectrometry data and elemental analyses are consistent with the proposed formula. Between room temperature and 173 K, the $^{31}P\{^1H\}$ NMR spectrum of **3** consists of a sharp singlet at $\delta = 49.9$ ppm ($^1J_{P,Pt} = 2113.5$ Hz). As expected, two sets of signals are present for the pyridyl groups in the $^{13}C\{^1H\}$ NMR spectrum.[8] It is noteworthy that heterobimetallic **3** is stable in CH_2Cl_2 solution for days; no signals corresponding to the Pd^{I} dimer **D^1** ($^{31}P\{^1H\}$ NMR: $\delta = 69.9$ ppm) or to the corresponding, hitherto-unknown Pt^{I} dimer are observed.

The proposed structure of **3** was confirmed by an X-ray diffraction study (Figure 2).[8] The dication of **3** contains two square-planar metal centers capped by two 2,5-bis(2-pyridyl)phosphole ligands acting as six-electron μ-1κN:1,2κP:2κN donors. The geometric parameters of the 2,5-bis(2-pyridyl)-phosphole ligands are almost identical for **3** and the corresponding homometallic Pd^{I} dimer **D^1**.[4] The metal–metal distance in **3** (2.7851(9) Å) is fairly long compared to typical Pd^{I}–Pt^{I} single bond lengths,[9] but is similar to that measured for the dipalladium complexes **D** (2.767(1)–2.787(1) Å).[4] The dication of **3** has a crystallographic center of symmetry at the midpoint of the metal–metal bond, which induces an equal occupancy of the Pd and Pt atoms at the two metal positions.[10] The metal–nitrogen bond lengths in **3** and **D^1** are essentially equal, although the geometry of the M_2P_2 core differs: for the homobimetallic complex **D^1** the P atoms bridge the two Pd^{I} centers symmetrically (Δ(μ-P–Pd) = 0.009(4) Å),[4] and the M_2P_2 core forms a diamond shape (**E** in Figure 2; $M^1 = M^2 =$ Pd), whereas in the heterodimer **3** each μ-P atom binds the two metal centers nonsymmetrically (Δ(μ-P–M) = 0.083(3) Å) and the M_2P_2 core adopts a dis-

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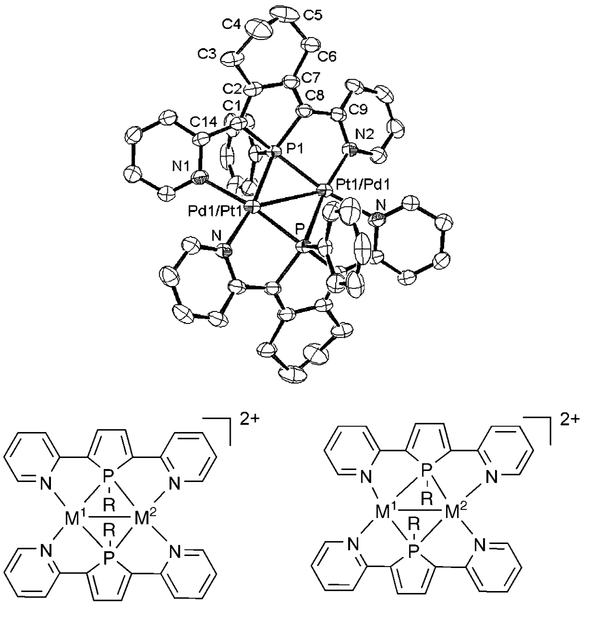


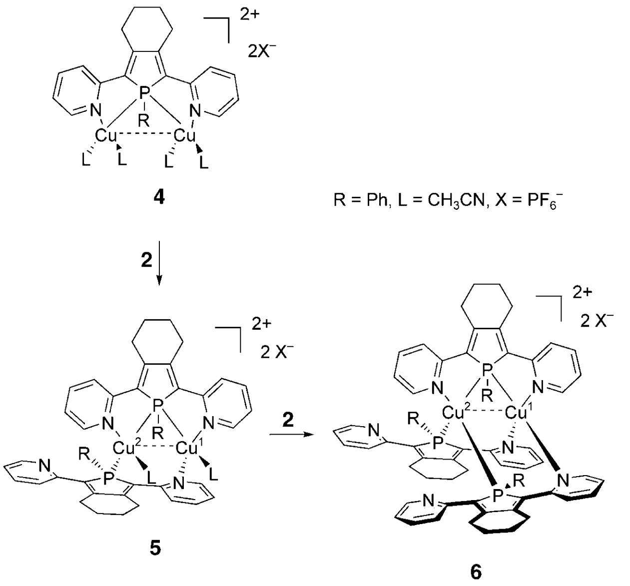
E: diamond structure **F**: distorted diamond structure

Figure 2. Molecular structure of the cation of complex **3** in the solid state (hydrogen atoms have been omitted for clarity; thermal ellipsoids at 50% probability). Selected bond lengths [Å]: P1–M1 2.3923(14), P1–M2 2.3091(15), N1–M1 2.160(5), N2–M2 2.142(4).

torted diamond shape (**F** in Figure 2; $M^1 = Pd$, $M^2 = Pt$). Hence, in spite of the tridentate coordination mode of the N,P,N-ligand **2**, the P atom can adopt a nonsymmetrical coordination mode. In fact, the μ-P centers of heterobimetallic **3** adopt a geometry that is intermediate between a symmetrically bridging (**A**) and a semi-bridging (**B**) coordination mode (Figure 1). This result suggests that there is no substantial discontinuity between these two coordination modes for μ-PR_3 ligands. In order to verify such a hypothesis, density functional theory calculations were carried out.[8]

The structure of heterobimetallic **3** was first optimized without symmetry constraints. The resulting structural arrangement matches the experimental structure with good accuracy.[8] The two phosphorus atoms are bound asymmetrically to the metal centers ($\Delta(\mu\text{-P–M}) \approx 0.09$ Å), which gives rise to the experimentally observed distorted diamond structure **F**. Geometry optimization of **3** by imposing a C_2 symmetry axis containing the metal atoms leads to the diamond structure **E.** Interestingly, the energy of **E** is very close to that of **F** ($\Delta E = 0.5$ kcal mol^{-1}).[11] Analogous results were obtained for the homometallic compound **D**^{1}: for example, the energies of structures **E** and **F** are almost the same ($\Delta E = 1.1$ kcal mol^{-1}). Obviously, there is a shallow and broad energy minimum around the symmetrical bridging position of the phosphorus atoms in this kind of complex. In other words, there is little energy cost for a bridging P center to move from a symmetrical to a substantially nonsymmetrical bridging position. Tiny changes such as the metal's electronic requirements, the environment about the metal, and/or the crystal packing can be invoked as the cause of the differences in structure between conformers **E** and **F**.

This conclusion was nicely confirmed by synthesis of a novel series of homobimetallic complexes in which two Cu^I atoms are tethered by a bridging phosphole. The reaction of di(2-pyridyl)phosphole (**2**) with $[Cu(CH_3CN)_4]PF_6$ (1:2 ratio) in CH_2Cl_2 at room temperature gives the dimetalated complex **4** (Scheme 2), which was isolated as an air-stable powder in 95% yield. In its ^{31}P NMR spectrum, besides the PF_6 signal ($\delta = -143.2$ ppm, $J_{P,F} = 704.1$ Hz), a singlet is observed at $\delta = -0.1$ ppm. Integration of the ^{1}H NMR spectrum suggests that **4** contains one di(2-pyridyl)phosphole and four acetonitrile ligands; the simple $^{13}C\{^1H\}$ NMR spectrum is in favor of a symmetric structure.[8] An X-ray diffraction study[8] revealed that compound **4** has the structure $[Cu_2(\mathbf{2})(CH_3CN)_4](PF_6)_2$ (Figure 3), in which two Cu^I atoms are capped by a 2,5-bis(2-pyridyl)phosphole ligand acting, again, as a six-electron μ-1κN:1,2κP:2κN donor. The Cu^I atoms have a distorted tetrahedral geometry due to the bite angle of the P,N-chelate



R = Ph, L = CH_3CN, X = PF_6^-

Scheme 2. Synthesis of Cu^I dimers **4**–**6**.

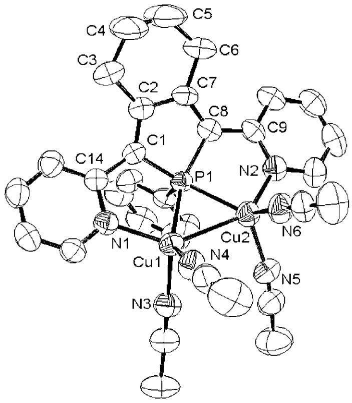


Figure 3. Molecular structure of the cation of complex **4** in the solid state (hydrogen atoms have been omitted for clarity; thermal ellipsoids at 50% probability).

(N1-Cu1-P1 = 85.29(12)°; N2-Cu2-P1 = 85.55(14)°), with a short intermetallic distance (2.568(10) Å).[12] The two Cu−N(pyridine) bond lengths are equal and the P atom adopts an almost symmetrical coordination mode (Δ(μ-P−Cu) = 0.010(2) Å; Table 1). Derivative **4** is the first complex in which two d^{10}-metal centers are bridged by a phosphane donor, and where two metals are held together by one bridging phosphane and no other supporting ligands (**C** is triply bridged and **D** is doubly bridged, Figure 1). These results suggest that bridging phosphane ligands are able to stabilize a large variety of bimetallic complexes and confirm that "*there is no inherent thermodynamic instability associated with this bonding situation*".[2a]

Table 1: Selected bond lengths [Å] for complexes **4**–**6**.

	4	5	6
Cu1−P1[a]	2.324(1)	2.293(1)	2.265(1)
Cu2−P1[a]	2.314(1)	2.387(1)	2.560(1)
Cu1−N1[a]	2.040(4)	2.047(4)	2.147(5)
Cu2−N2[a]	2.041(5)	2.043(4)	2.052(5)
Cu2−P2[b]	–	2.250(1)	2.299(1)
Cu2−P3[b]	–	–	2.296(1)
Cu1···Cu2	2.568(1)	2.5552(8)	2.6204(9)

[a] P1, N1, and N2 belong to the μ-1κN:1,2κP:2κN ligand; [b] P2 and P3 are the nonbridging P atoms.

The acetonitrile ligands of **4** can be displaced in CH_2Cl_2 solution by one or two equivalents of phosphole **2** to give complexes **5** (85% yield) and **6** (81% yield), respectively, which can be isolated as air-stable powders (Scheme 2).[8] An X-ray diffraction study[8] revealed that these dicationic Cu^I dimers still feature one 2,5-bis(2-pyridyl)phosphole ligand acting as a μ-1κN:1,2κP:2κN donor. The fact that the bridging coordination mode of the P center is retained upon addition of **2** to complex **4** highlights the robustness of bridging phosphanes as binucleating ligands. The tetrahedral geometry of the Cu^I atoms in **5** prevents the formation of a doubly bridged structure of type **D** (Figure 1), which requires square-planar metal centers. The dinuclear fragment of complexes **5** and **6** is bridged by one or two additional 1κP:2κN-chelates **2** (Scheme 2), respectively, the $Cu^I\cdots Cu^I$ separation being hardly perturbed with respect to that of complex **4** (Table 1). Note that the arrangement of the P,N-ligands in **6** (Scheme 2), which leads to two Cu atoms with either a "high-P" or "high-N" environment, is probably due to steric factors.

The series **4**–**6** gives the unique opportunity to study the evolution of the bridging coordination mode of a phosphane upon decreasing the local symmetry of the bimetallic core. It is striking to observe that the difference between the two μ-P−Cu distances increases continuously on going from **4** to **6** (Δ(μ-P−Cu): **4**, 0.010(2) Å; **5**, 0.094(2) Å ; **6**, 0.295(2) Å). The value of Δ(μ-P−M) found in complex **6** is typical for semi-bridged phosphanes,[5] with the longest P−Cu bond length always being observed for Cu2 (Scheme 2), which has a "high-P" environment (Table 1). Once again, the P atom of the N,P,N-pincer **2** can adopt a nonsymmetric bridging geometry. Moreover, these structural data confirm experimentally that there is no substantial discontinuity between symmetrical bridging (**A**) and semi-bridging (**B**) coordination modes for μ-PR_3 ligands (Figure 1). It is thus likely that these two coordination modes are shallow and broad minima on a flat potential energy surface. This situation is reminiscent of that of CO, the prototypical bridging ligand, and is a clue to understanding many of their key properties (e.g. fluxional behavior, bonding modes).[2a,3d,6]

These results show that chelates featuring bridging phosphanes are versatile binucleating ligands and that phosphanes have now to be considered as standard bridging ligands. The development of the robust Cu^I dimers **4** and **5** as building blocks for supramolecular architectures is under active investigation.

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[8] The Supporting Information includes NMR spectra (^1H and ^{13}C), mass spectra, and elemental analysis results for **3**, **4**, **5**, and **6**,

along with ORTEP views of the cations of complexes **5** and **6**, details of the X-ray crystal structure determinations, and theoretical calculations. CCDC-262841 (**3**), -262842 (**4**), -262843 (**5**), and -262844 (**6**) 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.

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[10] The two structures in which the Pd and Pt atoms are localized either at the M^1 or M^2 position are enantiomers. Hence, the equal occupancy of the two sites by a Pd or a Pt atom does not affect the coordinates of the P and N centers.

[11] This difference in energy is at the limit of accuracy of the method used. Moreover, structures **E** and **F** have similar HOMO–LUMO gaps (**E**: 1.553 eV; **F**: 1.556 eV).

[12] For a theoretical study of $[Cu_2(\mu\text{-}PH_3)_2(PH_3)_4]^{2+}$ see: P. A. Alemany, S. Alvarez, *Inorg. Chem.* **1992**, *31*, 4266. For recent papers on $Cu^I\cdots Cu^I$ interactions see: M. A. Carvajal, S. Alvarez, J. J. Novoa, *Chem. Eur. J.* **2004**, *10*, 2117; A. Vega, J.-Y. Saillard, *Inorg. Chem.* **2004**, *43*, 4012; S. Masaoka, D. Tanaka, Y. Nakanishi, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 2584; *Angew. Chem. Int. Ed.* **2004**, *43*, 2530.