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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Zhao, Chang-Qiu, Jennings, Michael C. and Puddephatt, Richard J. (2008) 'Coordination Chemistry of Tetrakis(diphenylphosphinomethyl)methane: Binuclear, Tetranuclear and Polymeric Complexes', *Journal of Coordination Chemistry*, 61: 1, 31 – 44

To link to this Article: DOI: 10.1080/00958970701700979

URL: <http://dx.doi.org/10.1080/00958970701700979>

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Coordination Chemistry of Tetrakis(diphenylphosphinomethyl)methane: Binuclear, Tetranuclear and Polymeric Complexes

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(Received 6 June 2007; in final form 23 August 2007)

The ligand tetrakis(diphenylphosphinomethyl)methane, tpmm, binds in a η^2, η^2 -bridging mode to square planar platinum(II) or palladium(II) centers to give complexes such as $[\text{Pt}_2\text{Me}_4(\mu\text{-tpmm})]$ or $[\text{Pd}_2\text{Cl}_4(\mu\text{-tpmm})]$. These complexes yielded triflate derivatives $[\text{Pt}_2\text{Me}_2(\text{OTf})_2(\mu\text{-tpmm})]$ or $[\text{Pd}_2(\text{OTf})_4(\mu\text{-tpmm})]$, and displacement of triflate by a bipyridine ligand then gave the cationic polymers $[\{\text{Pt}_2\text{Me}_2(\mu\text{-LL})(\mu\text{-tpmm})\}_n]^{2n+}$ or the cationic network materials $[\{\text{Pd}_2(\mu\text{-LL})_2(\mu\text{-tpmm})\}_n]^{4n+}$, LL = 4,4'-bipyridine or 1,3- $\text{C}_6\text{H}_4(\text{CONH}-4\text{-C}_5\text{H}_4\text{N})_2$. Ligand tpmm reacts with copper(I) iodide to give $[\text{Cu}_4\text{I}_4(\mu\text{-tpmm})_2]$ or with silver(I) triflate to give $[\text{Ag}_2(\text{OTf})_2(\mu\text{-tpmm})]$, which then reacts with LL = 1,3- $\text{C}_6\text{H}_4(\text{CONH}-4\text{-C}_5\text{H}_4\text{N})_2$ to give the polymeric complex $[\{\text{Ag}_2(\mu\text{-LL})(\mu\text{-tpmm})\}_n]^{2n+}$. The structure determination of $[\text{Cu}_4\text{I}_4(\mu\text{-tpmm})_2]$ shows that it contains two isomeric forms with the tpmm ligands in either the η^2, η^2 - or η^3, η^1 -bridging mode.

Keywords: tetrakisphosphine; platinum; copper; oligomer; polymer

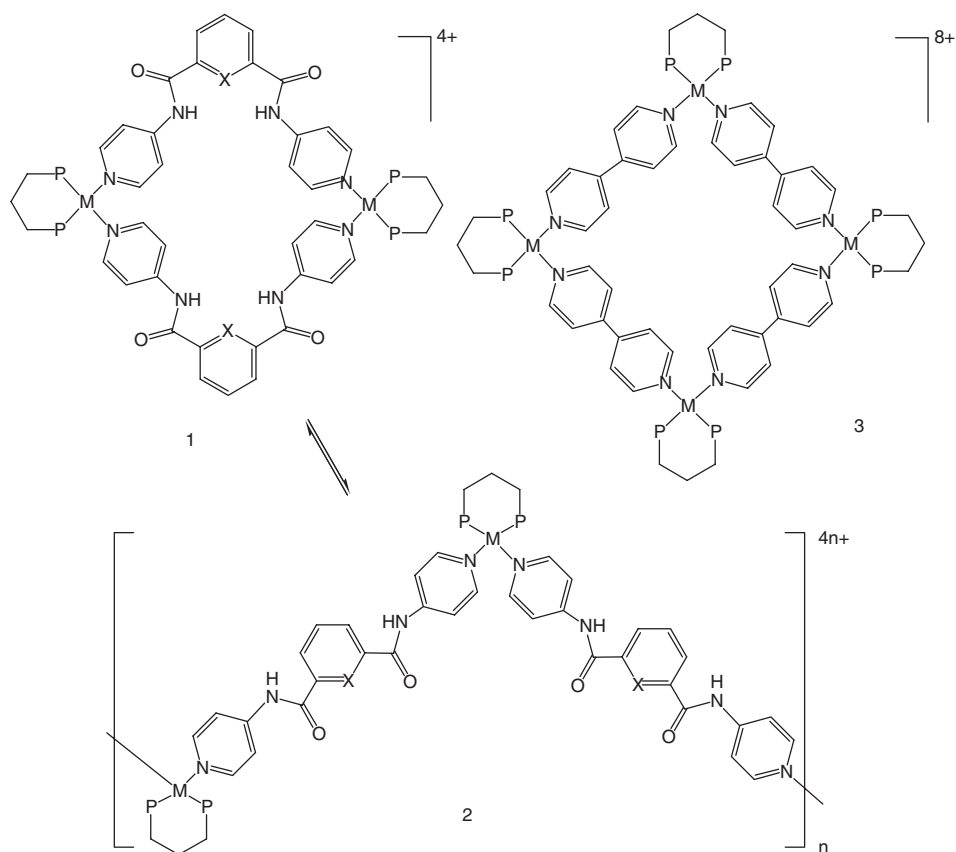
1. Introduction

There is much interest in self-assembly of molecular triangles, squares and polygons and also in the synthesis of metal-containing polymers [1–8]. One route to such compounds is to treat a *cis*-blocked palladium(II) or platinum(II) complex with a bipyridine or related ligand [1, 2, 8–10]. Typical examples are shown in scheme 1 ($\text{P} = \text{PPh}_2$, $\text{X} = \text{N}$ or CH , $\text{M} = \text{Pd}$ or Pt) [10–13]. If the ligand has some flexibility, the complex may self-assemble as a macrocycle such as **1** or as a polymer such as **2**, whereas, if the ligand is rigidly linear, the complex is more likely to self-assemble as a molecular square such as **3** (scheme 1) [10–13].

The ligand 1,3-bis(diphenylphosphino)propane, dppp, has been a versatile supporting ligand for studying the chemistry of self-assembly of the type shown in scheme 1 [10–13]. This paper reports some studies of self-assembly in coordination chemistry using the tetraphosphine ligand tetrakis(diphenylphosphinomethyl)methane,

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This paper is dedicated to Dr. Peter Williams in recognition of his contributions to both inorganic chemistry and the Journal of Coordination Chemistry

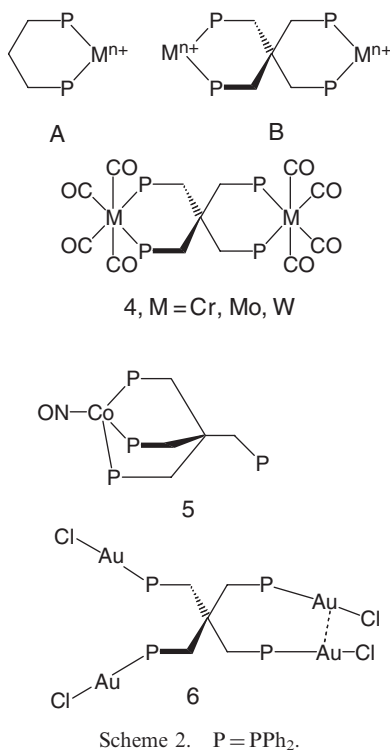


tpmm, which can be considered to comprise two dppp units fused at the γ -carbon atom [14–20] (compare structures **A** and **B** in scheme 2, P = PPh₂). If equivalent chemistry occurs, the macrocycle **1** or molecular square **3** with dppp supporting ligands should give a polymer of macrocycles or molecular squares respectively with tpmm supporting ligands, while the one-dimensional polymer **2** with dppp should give a sheet or network material with tpmm. However, it must be recognized that the above analogy with dppp, leading to an increase in dimensionality of equivalent structures, assumes that tpmm will always adopt the η^2, η^2 coordination mode, whereas known derivatives include the η^2, η^2 (**4**, scheme 2), the η^3, η^0 (**5**, scheme 2) and the $\eta^1, \eta^1, \eta^1, \eta^1$ (**6**, scheme 2) coordination modes [14–20].

2. Experimental

2.1. Synthesis and characterization

NMR spectra were recorded using a Varian Mercury 400 or Inova 400 MHz NMR spectrometer. ESI-MS were recorded using a Micromass LCT spectrometer in MeCN solution. The ligand tpmm and platinum complex [Pt₂Me₄(μ -SMe₂)₂] were



prepared according to the literature methods [20, 21]. NMR of tpmm in CD₂Cl₂: $\delta(^1\text{H}) = 2.33$ (s, 8H, CH₂); 7.18 (m, 40H, Ph); $\delta(^{31}\text{P}) = -27.2$ (s).

[Pt₂Me₄(μ -tpmm)], 7. To a solution of [Pt₂Me₄(μ -SMe₂)₂] (0.057 g, 0.1 mmol) in CH₂Cl₂ (2 mL) was added a solution of tpmm (0.081 g, 0.1 mmol) in CH₂Cl₂ (2 mL). After 30 min., the solvent was removed and the product was recrystallized from CH₂Cl₂/MeOH. Yield: 57%. Anal. Calc for C₅₇H₆₀P₄Pt₂: C, 54.4; H, 4.8. Found: C, 54.0; H, 4.6%. NMR in CD₂Cl₂: $\delta(^1\text{H}) = 0.26$ [m, 12H, J(PtH) = 69 Hz, MePt], 2.15 (m, 8H, CH₂); 7.1–7.3 (m, 40H, Ph); $\delta(^{31}\text{P}) = 3.39$ (s, J(PtP) = 2195 Hz, PtP). A similar reaction in 1:2 ratio gave a mixture of free tpmm, [Pt₂Me₄(μ -tpmm)], and [PtMe₂(tpmm)], **8**. NMR of [PtMe₂(tpmm)] in CD₂Cl₂: $\delta(^1\text{H}) = 0.09$ [m, 12H, J(PtH) = 69 Hz, MePt], 2.19 (m, 4H, CH₂); 2.32 (m, 4H, CH₂); 7.1–7.3 (m, 40H, Ph); $\delta(^{31}\text{P}) = -29.0$ (s, free P); 5.31 (s, J(PtP) = 2232 Hz, PtP).

[Pt₂Me₂(py)₂(tpmm)](OTf)₂, 10. To a solution of [Pt₂Me₄(μ -tpmm)] (0.063 g, 0.05 mmol) in CH₂Cl₂ (1 mL) was added triflic acid (74% solution in D₂O, 0.1 mmol), to generate [Pt₂Me₂(OTf)₂(tpmm)], **9**, in situ, followed by pyridine (0.2 mmol). The mixture was stirred at room temperature for 30 min., the solvents were evaporated, and the product was recrystallized from CH₂Cl₂/pentane. Yield 76%. Anal. Calc for C₆₇H₆₄F₆N₂O₆P₄Pt₂S₂: C, 47.7; H, 3.8; N, 1.7. Found: C, 47.3; H, 3.6; N, 1.5%. ESI-MS: $m/z = 1535$ [Pt₂Me₂(py)₂(tpmm)(OTf)⁺]. NMR in CD₂Cl₂: $\delta(^1\text{H}) = 0.28$ [m, 6H, J(PH) = 4, 7 Hz, J(PtH) = 53 Hz, MePt], 2.1–2.4 (m, 8H, CH₂); 7.1–8.3 (m, 50H, Ph, py); $\delta(^{31}\text{P}) = -1.17$ (d, J(PP) = 51 Hz, J(PtP) = 4449 Hz, PtP *trans* to py); 9.90 (d, J(PP) = 51 Hz, J(PtP) = 2019 Hz, PtP *trans* to Me).

[Pt₂Me₂(μ-4,4'-bipy)(tpmm)]_n(OTf)_{2n}, 11. To a solution of [Pt₂Me₄(μ-tpmm)] (0.063 g, 0.05 mmol) in CH₂Cl₂ (1 mL) was added triflic acid (74% solution in D₂O, 0.1 mmol) followed by 4,4'-bipyridine (0.1 mmol). The mixture was stirred at room temperature for 30 min., during which time the product precipitated as a white solid, which was separated, washed with ether, and dried under vacuum. Yield 62%. Anal. Calc for C₆₇H₆₂F₆N₂O₆P₄Pt₂S₂: C, 47.8; H, 3.7; N, 1.7. Found: C, 47.5; H, 3.5; N, 1.4%. ESI-MS: *m/z* = 1533 [Pt₂Me₂(bipy)(tpmm)(OTf)⁺]; 1689 [Pt₂Me₂(bipy)₂(tpmm)(OTf)⁺]; 3215 [Pt₄Me₄(bipy)₂(tpmm)₂(OTf)₃⁺]. NMR in CD₃CN: δ(¹H) = 0.25 [m, 6H, J(PtH) = 54 Hz, MePt], 2.1–2.3 (m, 8H, CH₂); 7.1–8.3 (m, 48H, Ph, bipy); δ(³¹P) = -1.41 (d, J(PP) = 55 Hz, J(PtP) = 4519 Hz, PtP *trans* to bipy); 9.79 (d, J(PP) = 55 Hz, J(PtP) = 2012 Hz, PtP *trans* to Me).

[Pt₂Me₂{μ-1,3-C₆H₄(CONH-4-C₅H₄N)₂}(tpmm)]_n(OTf)_{2n}, 12. This was prepared in a similar way but using 1,3-C₆H₄(CONH-4-C₅H₄N)₂ in place of 4,4'-bipy. Yield 63%. Anal. Calc for C₇₅H₆₈F₆N₄O₈P₄Pt₂S₂: C, 48.8; H, 3.7; N, 3.0. Found: C, 48.8; H, 3.4; N, 2.7%. NMR in CD₃CN: δ(¹H) = 0.30 [m, 6H, J(PH) = 3 Hz, 6 Hz, J(PtH) = 55 Hz, MePt], 2.1–2.3 (m, 8H, CH₂); 7.1–8.3 (m, 52H, Ph, C₆H₄, py); δ(³¹P) = -0.53 (d, J(PP) = 53 Hz, J(PtP) = 4470 Hz, PtP *trans* to bipy); 9.50 (d, J(PP) = 53 Hz, J(PtP) = 2000 Hz, PtP *trans* to Me).

[Pd₂Cl₄(tpmm)], 13. To a solution of [PdCl₂(COD)] (285.5 mg, 1 mmole) in CH₂Cl₂ (10 mL) was added a solution of tpmm (404 mg, 0.5 mmole) in CH₂Cl₂ (10 mL). A pale yellow solid formed immediately. The mixture was stirred for 2 h, and the product was separated, washed with CH₂Cl₂ and ether, and dried under vacuum. Yield: 96%. Anal. Calc for C₅₃H₄₈Cl₄P₄Pd₂: C, 54.7; H, 4.2. Found: C, 54.6; H, 3.9%.

[Pd₂(OTf)₄(tpmm)], 14. To a suspension of [Pd₂Cl₄(tpmm)] (540 mg, 0.46 mmol) in acetonitrile (25 mL) was added a solution of AgOTf (520 mg, 2 mmol) in acetonitrile (10 mL). The mixture was stirred for 48 h., filtered to remove insoluble material, and the solvent was evaporated from the filtrate to give the product, which was recrystallized from CH₂Cl₂/ether. Yield: 93%. NMR in CD₃CN: δ(¹H) = 2.55 (d, 8H, J(PH) = 6 Hz, CH₂); 7.5–7.8 (m, 40H, Ph); δ(³¹P) = 22.19 (s, PdP).

[Pd₂{μ-1,3-C₆H₄(CONH-4-C₅H₄N)₂}(tpmm)]_n(OTf)_{4n}, 15. A mixture of [Pd₂(OTf)₄(tpmm)] (32.4 mg, 0.02 mmol) and 1,3-C₆H₄(CONH-4-C₅H₄N)₂ (12.8 mg, 0.04 mmol) in acetonitrile (10 mL) was stirred for 5 h. The resulting colorless solution was filtered, the volume of the filtrate was reduced to 1 mL, and ether (10 mL) was added to precipitate the product as a white solid, which was washed with ether, and dried under vacuum. Yield: 82%. Anal. Calc for C₉₃H₇₆F₁₂N₈O₁₆P₄Pd₂S₄: C, 49.5; H, 3.4; N, 5.0. Found: C, 49.8; H, 3.4; N, 4.6%. NMR in CD₃CN: δ(¹H) = 2.3 (m, 8H, CH₂); 7.1–8.3 (m, 64H, Ph, C₆H₄, py); δ(³¹P) = 18.5 (br, PdP).

[Pd₂(μ-4,4'-bipy)₂(tpmm)]_n(OTf)_{4n}, 16. This was prepared in a similar way but using 4,4'-bipyridine. Yield: 70%. Anal. Calc for C₇₇H₆₄F₁₂N₄O₁₂P₄Pd₂S₄: C, 47.9; H, 3.3; N, 2.9. Found: C, 47.4; H, 3.1; N, 2.6%. ESI-MS: *m/z* = 1779 [Pd₂(bipy)₂(tpmm)(OTf)₃⁺]; 1935 [Pd₂(bipy)₃(tpmm)(OTf)₃⁺]; 3707 [Pd₄(bipy)₄(tpmm)₂(OTf)₇⁺]. NMR in CD₃CN: δ(¹H) = 2.4 (m, 8H, CH₂); 7.1–8.3 (m, 56H, Ph, bipy); δ(³¹P) = 19.6 (br, PdP).

[Cu₂I₂(tpmm)], 17. To a solution of tpmm (40.4 mg, 0.05 mmol) in DMSO (1 mL) and CH₂Cl₂ (1 mL) was added CuI (19 mg, 0.1 mmol) in acetonitrile (1 mL). The clear

colorless solution which formed was stirred for 2 h., then ether (10 mL) was added to precipitate the product as a white solid. Yield: 65%. Anal. Calc for $C_{53}H_{48}Cu_2I_2P_4$: C, 53.5; H, 4.1. Found: C, 53.8; H, 3.9%. NMR in CD_3CN : $\delta(^1H) = 2.4$ (br, 8H, CH_2); 7.1–7.5 (m, 40H, Ph); $\delta(^{31}P) = -6.5$ (br, CuP).

[Ag₂(OTf)₂(tpmm)], 18. To a solution of tpmm (40 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was added AgOTf (104 mg, 0.1 mmol) in acetone (3 mL). The mixture was stirred for 30 min., then ether (10 mL) was added to precipitate the product as a white solid. Yield: 87%. Anal. Calc for $C_{55}H_{48}Ag_2F_6O_6P_4S_2$: C, 49.9; H, 3.7. Found: C, 49.7; H, 3.3%. NMR in CD_3CN : $\delta(^1H) = 2.6$ (br, 8H, CH_2); 7.1–7.5 (m, 40H, Ph); $\delta(^{31}P) = -8.8$ (br, AgP).

[Ag₂{1,3-C₆H₄(CONH-4-C₅H₄N)₂}(tpmm)_n(OTf)_{2n}], 19. A mixture of [Ag₂(OTf)₂(tpmm)] (26 mg, 0.02 mmol) and 1,3-C₆H₄(CONH-4-C₅H₄N)₂ (6.4 mg, 0.02 mmole) in acetonitrile (1 mL) and methanol (2 mL) was stirred for 16 h. The solution was filtered, the volume was reduced to 0.5 mL under vacuum, and ether (10 mL) was added to precipitate the product as a white solid. Yield: 40%. Anal. Calc for $C_{73}H_{62}Ag_2F_6N_4O_8P_4S_2$: C, 53.4; H, 3.8; N, 3.4. Found: C, 53.9; H, 4.1; N, 3.8%. NMR in CD_3CN/CD_3OD : $\delta(^1H) = 2.8$ (br, 8H, CH_2); 7.2–8.6 (m, 52H, aromatic); $\delta(^{31}P) = -4.4$ (br, AgP).

2.2. X-ray structure determination

Crystals of $[Cu_4I_4(\mu\text{-tpmm})_2] \cdot MeCN$ were grown from acetonitrile solution. A colorless plate was mounted on a glass fiber. Data were collected at $-123^\circ C$ using a Nonius Kappa-CCD diffractometer with COLLECT software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO and the data were scaled using SCALEPACK. The crystal data and refinement parameters are listed in table 1. The reflection data indicated the triclinic space group P(1), and this was confirmed by successful refinement: an attempt to refine the structure in space group P(-1) was unsuccessful. The SHELXTL-NT V6.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. The molecule was disordered, such that P(5) was bonded to Cu4 or Cu3. Cu3, Cu4, and P5 were each modeled as a 50/50 disorder and refined anisotropically. The carbon atoms of the disorder were modeled isotropically. There were two MeCN solvate molecules, and each was modeled as $\frac{1}{2}$ occupancy, with isotropic atoms. The bond lengths were fixed (N–C 1.14 Å, C–C 1.47 Å, N...C 2.61 Å). Unless mentioned otherwise, all of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and included as riding on their respective carbon atoms. The Flack parameter refined to 0.55(3), indicating the presence of inversion twinning.

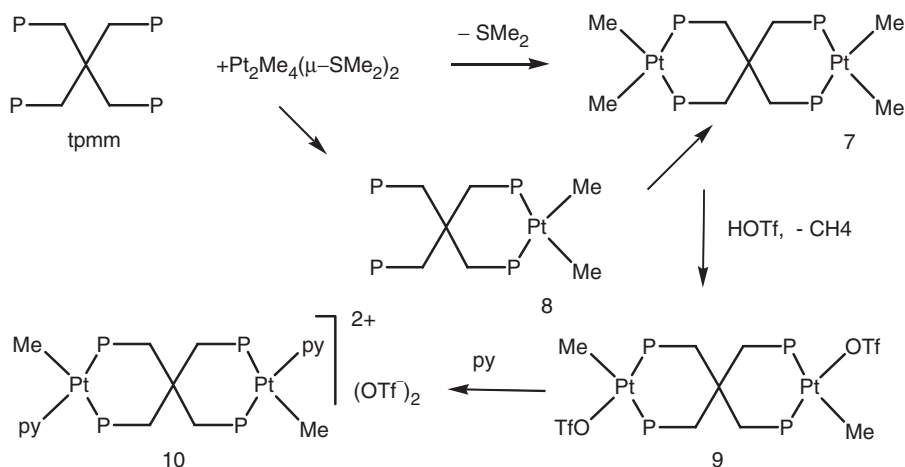
3. Results and Discussion

3.1. Organoplatinum polymers and model compounds

Reaction of tpmm with $[Pt_2Me_4(\mu\text{-SMe}_2)_2]$ [20, 21] in a 1 : 1 ratio occurred easily to give the *bis*(dimethylplatinum)(II) complex $[Pt_2Me_4(\mu\text{-tpmm})]$, 7 (scheme 3). The 1H NMR

Table 1. Crystal data and structure refinement for $[\text{Cu}_4\text{I}_4(\mu\text{-tpmm})_2] \cdot \text{MeCN}$.

Formula, fw	$\text{C}_{108}\text{H}_{99}\text{Cu}_4\text{I}_4\text{NP}_8$, 2420.40
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions (Å, °)	
<i>a</i>	10.7177(3)
<i>b</i>	12.6158(4)
<i>c</i>	20.7860(7)
α	80.5200(10)
β	87.1530(10)
γ	68.274(2)
Volume (Å ³)	2575.03(14) ³
<i>Z</i>	1
Density (calculated)	1.561 Mg m ⁻³
Absorption coefficient	2.184 mm ⁻¹
Absorption correction	Integration
Data/restraints/parameters	13557/9/922
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	$R_1 = 0.0530$, $wR_2 = 0.1193$
Absolute structure parameter	0.55(3)



spectrum contained a single methylplatinum resonance as an $A_3A'_3XX'$ multiplet due to coupling with the adjacent ^{31}P atoms and with coupling constant to ^{195}Pt $^2J(\text{PtH}) = 69$ Hz, typical of complexes with *cis*-PtMe₂P₂ coordination [23–25]. The high symmetry of the complex was also confirmed by observation of a single CH₂ resonance in the ^1H NMR spectrum, and a single resonance in the ^{31}P NMR spectrum with coupling constant $^1J(\text{PtP}) = 2195$ Hz, typical of complexes of this type [24, 25]. A similar reaction in 2 : 1 ratio gave a mixture of free tpmm, $[\text{Pt}_2\text{Me}_4(\mu\text{-tpmm})]$, and the unsymmetrical complex $[\text{PtMe}_2(\text{tpmm})]$, **8**, in which the tpmm ligand is bidentate to a single dimethylplatinum(II) unit. It was not possible to separate **7** and **8**, but **8** could be identified by its NMR spectra. The ^1H NMR spectrum contained a single

methylplatinum resonance, but two resonances for the CH₂ groups of the ligand. The ³¹P NMR spectrum of **8** contained two equal intensity resonances for the free and coordinated phosphorus atoms. None of the presumed intermediate **8** was observed when reaction of tpmm with [Pt₂Me₄(μ-SMe₂)₂] was carried out in a 1:1 ratio, and the reaction to give **7** appears to occur quantitatively.

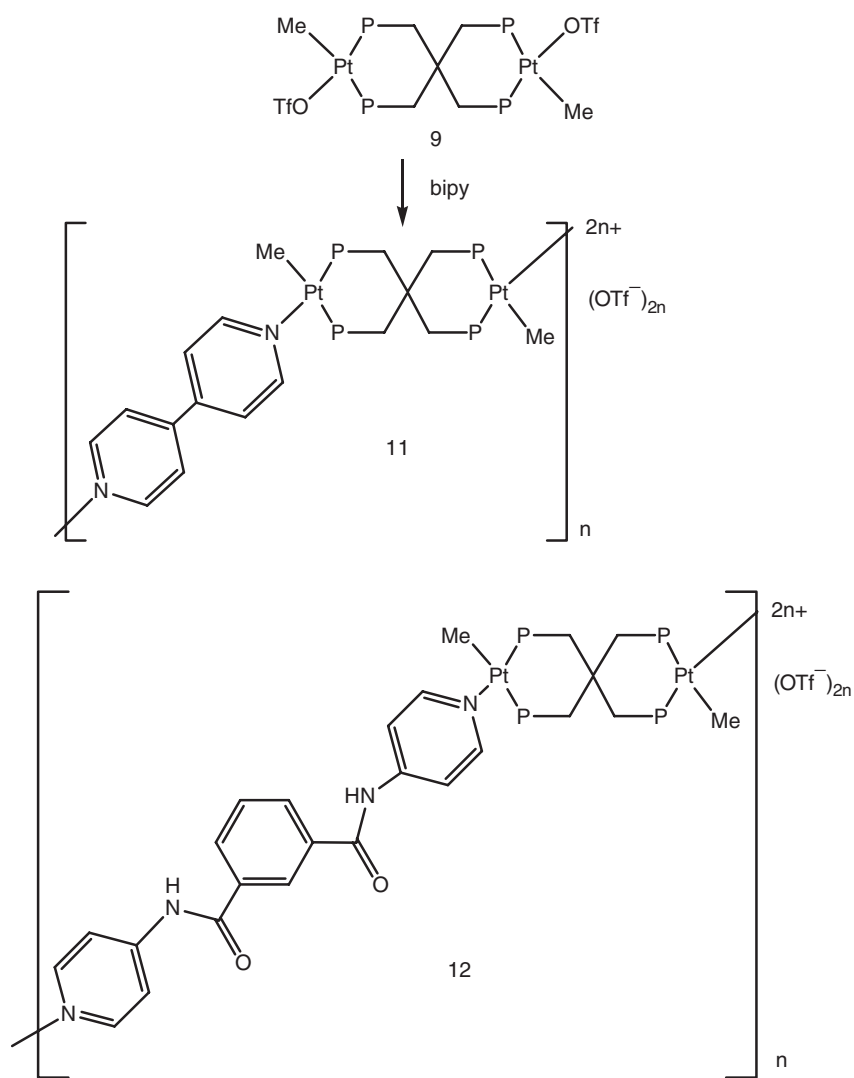
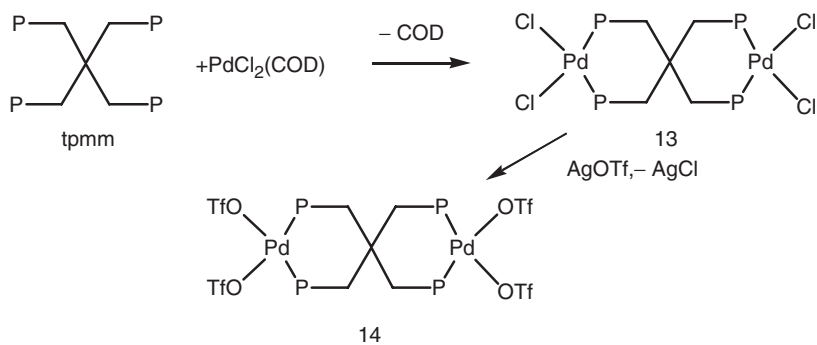
The reaction of **7** with triflic acid gave a complex tentatively identified as **9** (scheme 3), but this complex could not be isolated in pure form and its NMR spectra were broad and poorly resolved. Similar complexes are fluxional as a result of easy displacement of triflate ligands by solvent or water molecules [26]. Nevertheless, if **9** was generated *in situ* and then treated with pyridine, the cationic complex [Pt₂Me₂(py)₂(tpmm)](OTf)₂, **10** could be isolated in pure form. Complex **10** has approximately C₂ symmetry. In the ¹H NMR spectrum, there was a single methylplatinum resonance, which appeared as a doublet of doublets due to coupling to the *cis* and *trans* phosphorus atoms [$\delta(\text{MePt})=0.28$, $^3\text{J}(\text{PH})=4$ Hz, 7 Hz, $^2\text{J}(\text{PtH})=53$ Hz], and the non-equivalent CH₂ resonances were overlapped in the region $\delta=2.1\text{--}2.4$ (four resonances are expected). The ³¹P NMR spectrum of **10** contained two equal intensity resonances for the phosphorus atoms *trans* to methyl [$\delta=9.90$, J(PP)=51 Hz, J(PtP)=2019 Hz,] and pyridine [$\delta=-1.17$, J(PP)=51 Hz, J(PtP)=4449 Hz] respectively. The ESI-MS contained an envelope of peaks at $m/z=1535$, assigned as [Pt₂Me₂(py)₂(tpmm)(OTf)]⁺, which supports the proposed structure. Complex **10** is a model for the polymeric complexes described below.

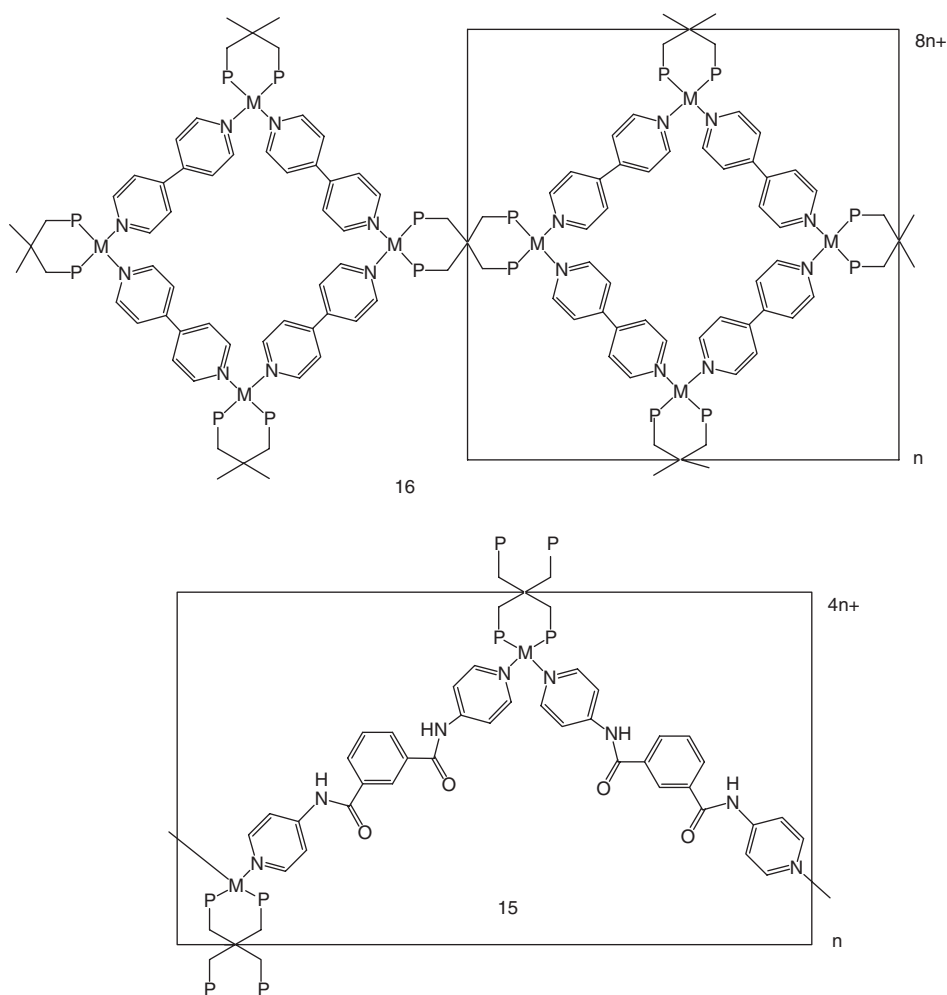
Reaction of **9**, generated *in situ* as above, with 4,4'-bipyridine or 1,3-C₆H₄(CONH-4-C₅H₄N)₂ gave the corresponding polymeric complexes [Pt₂Me₂(μ-4,4'-bipy)(tpmm)]_n(OTf)_{2n}, **11**, or [Pt₂Me₂{μ-1,3-C₆H₄(CONH-4-C₅H₄N)₂}(tpmm)]_n(OTf)_{2n}, **12**, respectively (scheme 4). Complexes **11** and **12** were insoluble in non-polar solvents, but sufficiently soluble in acetonitrile to give satisfactory NMR spectra. These spectra were similar to, but broader than, those of the model binuclear complex **10**. For example, complex **11** gave $\delta(\text{MePt})=0.25$, J(PtH)=54 Hz and $\delta(^{31}\text{P})=-1.41$ [J(PP)=55 Hz, J(PtP)=4519 Hz, PtP *trans* to bipy] and 9.79 [J(PP)=55 Hz, J(PtP)=2012 Hz, PtP *trans* to Me]. The ESI-MS of **11** showed peak envelopes due to diplatinum complexes at $m/z=1534$ and 1690 assigned to [Pt₂Me₂(bipy)(tpmm)(OTf)]⁺ and [Pt₂Me₂(bipy)₂(tpmm)(OTf)]⁺, and a low intensity peak at $m/z=3215$ assigned to the tetraplatinum unit [Pt₄Me₄(bipy)₂(tpmm)₂(OTf)₃⁺].

3.2. Palladium polymers and molecular squares

Reaction of tpmm with [PdCl₂(COD)] (COD=1,5-cyclooctadiene) gave the palladium(II) chloride derivative [Pd₂Cl₄(tpmm)], **13**, as an insoluble yellow solid (scheme 5), and further reaction of **13** with silver triflate gave the more soluble triflate derivative, [Pd₂(OTf)₄(tpmm)], **14**. The ¹H NMR spectrum of **14** contained a single resonance for the CH₂ protons of the ligand [$\delta(\text{CH}_2)=2.55$, $^2\text{J}(\text{PH})=6$ Hz] and there was a single resonance in the ³¹P NMR spectrum [$\delta(^{31}\text{P})=22.19$].

Complex **14** reacted easily with 1,3-C₆H₄(CONH-4-C₅H₄N)₂ or with 4,4'-bipyridine to give [Pd₂{μ-1,3-C₆H₄(CONH-4-C₅H₄N)₂}(tpmm)]_n(OTf)_{4n}, **15**, or [Pd₂(μ-4,4'-bipy)₂(tpmm)]_n(OTf)_{4n}, **16**, respectively (scheme 6). By analogy with **2** and **3** (scheme 1) [10–13], and assuming that tpmm will give higher dimensionality than dppp [20], **15** is expected to form a sheet or network material while **16** is expected to

Scheme 4. P = PPh₂.Scheme 5. P = PPh₂.

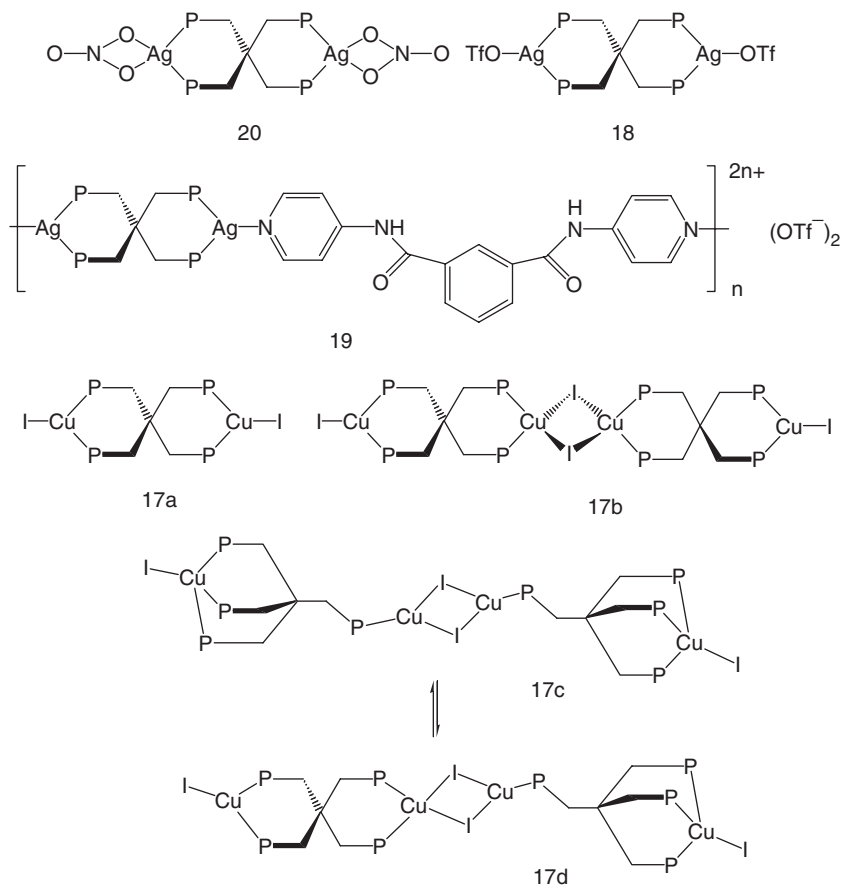
Scheme 6. P = PPh₂.

exist as a sheet of molecular squares. Each molecular square in **16** should have four neighboring squares which will be roughly orthogonal to it as a result of the orientation of the phosphorus donors in the tpmm ligands. Only one of these neighbors is shown in full in scheme 6, but the expected 4-fold symmetry is indicated by the repeat unit in the box. Unfortunately it has not been possible to grow suitable single crystals to determine the solid state structure by experiment. The complexes are insoluble in non-polar organic solvents but they do have limited solubility in dmsO or acetonitrile. Each gave broad NMR spectra, and the ³¹P NMR spectra showed a single broad resonance in each case (see experimental section).

3.3. Complexes of copper(I) and silver(I)

Some complexes of tpmm with silver(I) and gold(I) have been reported previously [19, 20]. In particular, the binuclear nature of complex **20** (scheme 7) was confirmed by

molecular weight determination in solution [19]. This article reports related copper(I) iodide and silver(I) triflate derivatives, $[\text{Cu}_2\text{I}_2(\text{tpmm})]$, **17** and $[\text{Ag}_2(\text{OTf})_2(\text{tpmm})]$, **18**. These new complexes were prepared by simple combination of tpmm with copper(I) iodide or silver(I) triflate in the required ratio. Attempts to prepare the copper(I) triflate complex were unsuccessful. The structure of the silver(I) complex **18** is likely to be similar to that of the nitrate derivative **20** [19], although this conclusion is tentative because the nature of binding of the triflate anions in **18** is not known. Both **17** and **18** give a broad singlet in the ^{31}P NMR spectra. For **18**, no coupling $^1J(\text{AgP})$ was resolved, indicating that the complex is fluxional but **18** was insufficiently soluble to allow a study of this process by variable temperature NMR. A clue to the nature of the fluxionality is provided by the solid state structure of the copper(I) complex **17**, which is described below. The simplest structure for **17** is the binuclear structure **17a**, but it might be expected to oligomerize or polymerize through iodide bridging as shown in **17b** (scheme 7). Surprisingly, in the solid state, there is disorder between the structures **17c** and **17d** (scheme 7), in which one of the tpmm ligands may bind as an η^2, η^2 or as an η^3, η^1 ligand, while the other is η^3, η^1 . Reaction of **18** with 1,3- $\text{C}_6\text{H}_4(\text{CONH}-4-\text{C}_5\text{H}_4\text{N})_2$ gave the polymeric complex $[\text{Ag}_2\{1,3-\text{C}_6\text{H}_4(\text{CONH}-4-\text{C}_5\text{H}_4\text{N})_2\}(\text{tpmm})]_n(\text{OTf})_{2n}$, **19**.



Scheme 7. P = PPh_2 .

Complex **19** was insoluble in non-polar solvents but sufficiently soluble in a mixture of CD₃CN/CD₃OD to give an NMR spectrum. The ³¹P NMR spectrum contained a broad singlet at $\delta = -4.4$, again indicating fluxionality in which the phosphorus atoms dissociate reversibly from a given silver(I) center.

3.4. Structure of the copper(I) complex **17**

The structure of complex **17** is shown in figure 1 and selected bond distances are given in table 2. The complex is a dimer of [Cu₂I₂(tpmm)] units by formation of a Cu₂(μ -I)₂ bridging unit, and so complex **17** should be considered as [Cu₄I₂(μ -I)₂(tpmm)₂]. Association of copper(I) halide derivatives through halide bridges is well-known [27–29]. Complex **17** exhibits an unusual form of disorder in which 50% of the molecules have the structure **17c** (scheme 7) in which both ligands are η^3, η^1 -tpmm (figure 1b), while the other 50% have structure **17d** (scheme 7) in which one ligand is η^3, η^1 -tpmm and the other is η^2, η^2 -tpmm (figure 1c). In **17c** the phosphorus donor P(5A) is coordinated to Cu(4A) whereas in **17d** this arm of the ligand flips over so that P(5B) is coordinated to Cu(3B). The coordination numbers of Cu(3) and Cu(4) are thus different in the two components [Cu(3A) and Cu(4B) are three-coordinate, while Cu(3B) and Cu(4A) are four-coordinate] and so the positions of these copper atoms are different in the two components (see figure 1a). Complex **17** appears to be the first example of a tpmm complex in which the ligand binds in the η^3, η^1 -tpmm form [14–20].

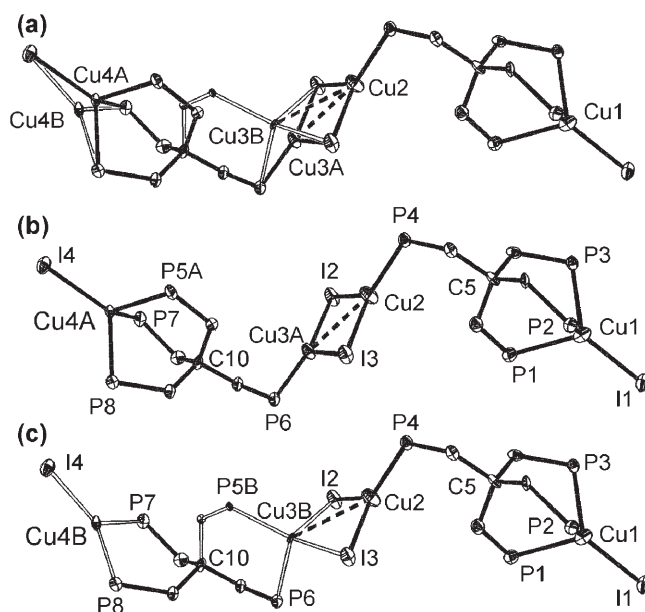


Figure 1. The structure of [Cu₄I₂(μ -I)₂(tpmm)₂], with phenyl groups omitted for clarity: (a) the disorder model showing both components of the tpmm ligand which bridges between Cu(3) and Cu(4); (b) the component **17c** in which both ligands are η^3, η^1 -tpmm; (c) the component **17d** in which one ligand is η^3, η^1 -tpmm and the other is η^2, η^2 -tpmm.

Table 2. Selected bond distances (Å) for complex **17**.

Molecule 17c		Molecule 17d	
Cu(1)–P(1)	2.340(5)	Cu(1)–P(1)	2.340(5)
Cu(1)–P(2)	2.275(4)	Cu(1)–P(2)	2.275(4)
Cu(1)–P(3)	2.267(5)	Cu(1)–P(3)	2.267(5)
Cu(1)–I(1)	2.535(2)	Cu(1)–I(1)	2.535(2)
Cu(2)–P(4)	2.179(5)	Cu(2)–P(4)	2.179(5)
Cu(2)–I(2)	2.513(2)	Cu(2)–I(2)	2.513(2)
Cu(2)–I(3)	2.575(2)	Cu(2)–I(3)	2.575(2)
Cu(2)–Cu(3A)	2.633(3)	Cu(2)–Cu(3B)	2.848(3)
Cu(3A)–P(6)	2.145(6)	Cu(3B)–P(6)	2.380(5)
Cu(3A)–I(2)	2.576(4)	Cu(3B)–I(2)	2.643(3)
Cu(3A)–I(3)	2.444(4)	Cu(3B)–I(3)	2.745(3)
Cu(4A)–P(5A)	2.316(9)	Cu(3B)–P(5B)	2.173(5)
Cu(4A)–P(7)	2.261(5)	Cu(4B)–P(7)	2.279(5)
Cu(4A)–P(8)	2.317(6)	Cu(4B)–P(8)	2.218(5)
I(4)–Cu(4A)	2.561(4)	I(4)–Cu(4B)	2.429(3)

There are precedents for the stereochemistries of the individual copper(I) centers in **17**, though the combination for the four copper(I) centers appears to be unprecedented. Complexes of the form LCuX (L = phosphine ligand, X = halide) usually adopt halide bridged structures [27–29]. These may be complex in nature [27, 28] or relatively simple as found for Cu(2) and Cu(3A) in **17c** and Cu(2) in **17d** (figure 1) [27–29]. Complexes L₃CuX do not form halide bridges because the copper(I) centers are coordinatively saturated [30, 31], and so the centers Cu(1) and Cu(4A) in **17c** or Cu(1) in **17d** are typical. The complexes [MeC(CH₂PPh₂)₃CuX] are particularly close analogs for the CuIP₃ centers in **17** [31]. Complexes L₂CuX most commonly form halide bridges as seen for Cu(3B) in **17d** (figure 1), but they may not do so if the phosphine ligand L is bulky and Cu(4B) in **17d** falls into this class of copper(I) center. In general, bond distances to copper(I) increase with increasing coordination number, and this trend can be seen by comparing distances in **17c** and **17d** (table 2). For example, the distance Cu(4B)–I(4) in **17d** is shorter than Cu(4A)–I(4) in **17c**, whereas the distances Cu(3A)–I(2) and Cu(3A)–I(3) in **17c** are shorter than Cu(3B)–I(2) and Cu(3B)–I(3) in **17d** (table 2).

4. Conclusions

This work has shown that in binding to square planar palladium(II) or platinum(II) centers, tpmm always adopts the η^2, η^2 bridging mode. With the ligand in this bridging mode, the platinum(II) or palladium(II) complexes are particularly well suited to form macrocycles, molecular squares or polymers with bis(pyridine) ligands. Evidence, based primarily on analytical data and NMR spectroscopy, suggests that the structures formed are analogous to those formed by 1,3-bis(diphenylphosphino)propane, dppp, but with extra dimensionality in the bridging tpmm derivatives. One limitation on the chemistry is that the polymeric and network materials have low solubility and are difficult to crystallize, and so the characterization is not definitive.

When tpmm binds to a d¹⁰ metal ion with varying coordination number, such as copper(I), silver(I) or gold(I), the binding is more versatile [19, 20]. In this work,

the structure of the copper(I) iodide complex **17** is shown to contain tpmm in the η^3, η^1 bridging mode as well as in the known η^2, η^2 bridging mode [19]. The ^{31}P NMR spectrum of **17** contains only a single broad resonance whereas several resonances would be expected for the non-equivalent phosphorus atoms in the solid state structure (figure 1). We suggest that easy fluxionality occurs by reversible dissociation/coordination of individual phosphorus donors, leading to equilibration between isomers such as **17c** and **17d** (scheme 7, figure 1) and exchanging phosphorus donors between the central and peripheral copper(I) centers. Similar fluxionality might also occur with the silver(I) complexes, explaining the loss of the expected $^1\text{J}(\text{AgP})$ couplings.

Overall, tpmm is shown to have promise in forming molecular materials by increasing the dimensionality of analogous complexes formed by dppp.

Supplementary material

Crystallographic data for the structure in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC 649976. The data can be obtained, free of charge, at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the NSERC (Canada) for financial support and the Government of Canada for a Canada Research Chair to RJP.

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