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One-dimensional silver(I) coordination polymers containing cyclodiphosphazane, *cis*-$\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\}_2$

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Received 21st March 2007, Accepted 11th May 2007
First published as an Advance Article on the web 30th May 2007
DOI: 10.1039/b704303a

The 1 : 1 reaction between the cyclodiphosphazane *cis*-$\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\}_2$ (**1**) and AgOTf afforded one-dimensional Ag^{I} coordination polymer $[\text{Ag}\{\mu\text{-OTf-}\kappa O,\kappa O\}\{\mu\text{-}(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\text{-}\kappa P,\kappa P\}_2]_\infty$ (**2**) containing bridging cyclodiphosphazane and trifluoromethanesulfonate (OTf) ligands. The 2 : 1 reaction of **1** and AgOTf leads to the formation of simple mononuclear complex $[\text{Ag}\{\text{OTf-}\kappa O,\kappa O\}(\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\text{-}\kappa P\}_2)_2]$ (**3**) in quantitative yield. Reaction of **1** with AgCN produces a strain-free zig-zag coordination polymer $[(\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\text{-}\kappa P,\kappa P\}_2)_2\text{Ag(NCAgCN)}]_\infty$ (**4**) irrespective of reaction stoichiometry and conditions. In complexes **3** and **4** cyclodiphosphazanes coordinate to Ag^{I} centers in a monodentate fashion. Single crystal structures were established for the Ag^{I} polymers **2** and **4**.

Introduction

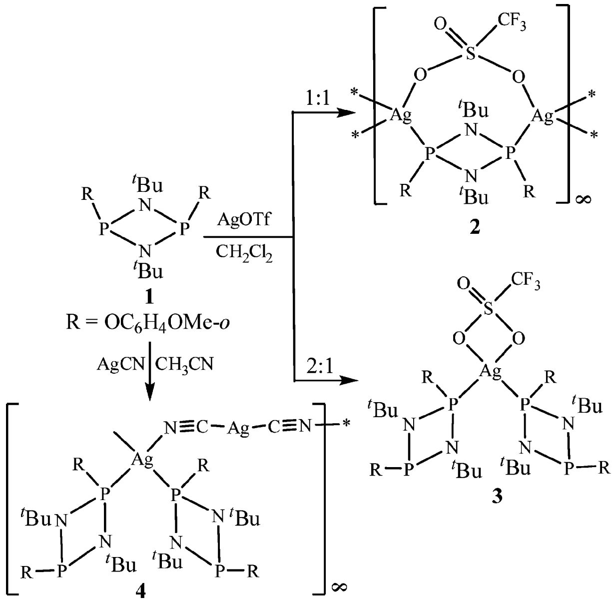
Rigid bridging multidentate ligands have been extensively used for the construction of 1-D to 3-D metallopolymers and other interesting self assemblies.[1] These supramolecular complexes show applications in catalysis, sensors, gas storage, as well as in nanoscience.[2] A variety of rigid multidentate ligands containing nitrogen and/or sulfur donors have been designed and used in supramolecular coordination chemistry,[3] one significant example being 4,4′-bipyridine and related systems.[4] Although phosphorus-donor ligands can stabilize a wide range of soft metal centers, their utility for the construction of supramolecular and polymeric structures is limited due to the non-availability of rigid ligand frameworks with donor centers in favorable orientations.[5]

We have recently been exploring the reactivity and the transition metal chemistry of cyclodiphosphazanes with donor functionalities.[6] The ability of these rigid four-membered P_2N_2 rings to act as 2e, 4e, 6e or 8e donors through various coordination modes has resulted in the formation of species ranging from simple mononuclear complexes to multinuclear clusters and coordination polymers. These interesting results prompted us to use these four-membered P_2N_2 ring systems with Group 11 metals which exhibit attractive coordination architectures ranging from simple complexes to multinuclear cages and coordination polymers. Although Ag^{I} coordination polymers containing rigid sulfur and nitrogen donor ligands are known,[7] analogous compounds containing phosphorus donors are less extensive. In this article, we report two novel Ag^{I} coordination polymers with the cyclodiphosphazane *cis*-$\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\}_2$ (**1**) showing both the monodentate and the bridged bidentate coordination modes.

Results and discussion

Synthesis and characterization

Reaction of *cis*-$\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\}_2$ (**1**) with AgOTf in a 1 : 1 stoichiometry in dichloromethane at room temperature affords the Ag^{I} coordination polymer $[\text{Ag}\{\mu\text{-OTf-}\kappa O,\kappa O\}\{\mu\text{-}(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\text{-}\kappa P,\kappa P\}_2]_\infty$ (**2**) in 73% yield. Under similar reaction conditions 2 : 1 reaction between **1** and AgOTf produces mononuclear silver(I) complex $[\text{Ag}\{\text{OTf-}\kappa O,\kappa O\}(\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\text{-}\kappa P\}_2)_2]$ (**3**) as shown in Scheme 1. The ^{31}P NMR spectrum of **2** exhibits a broad signal at 116.6 ppm, whereas compound **3** exhibits two broad signals at 139.9 ppm and 112.8 ppm, respectively, for uncoordinated and coordinated P centers of cyclodiphosphazane. The IR spectrum of each of



Scheme 1 Synthesis of silver(I) complex of cyclodiphosphazane.

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complexes **2** and **3** show $\nu(SO_3)$ around 1256 cm^{-1} and 1028 cm^{-1} which clearly indicates the bidentate(*O*,*O*) mode of coordination of the triflate anion.[8] The mass spectrum of **3** shows a peak at m/z 1009.00, which corresponds to the (M − OTf) ion.

Reaction of **1** with AgCN in acetonitrile produces a strain-free zig-zag polymer, $[(\{\mu\text{-}(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)\text{-}\kappa P\}_2)_2Ag(NCAgCN)]_\infty$ (**4**), irrespective of the stoichiometry of the reactants and the reaction conditions. In complex **2**, the cyclodiphosphazane exhibits a bridging coordination mode whereas the monodentate mode of coordination was observed in complexes **3** and **4**. Complex **4** is stable in both solid and solution states and is soluble in CH_3CN, CH_3COCH_3, DMSO and partially soluble in THF and CH_2Cl_2. The ^{31}P NMR spectrum of **4** shows a single resonance at 137.2 ppm even at −50 °C. Two different ^{31}P signals are expected for complex **4** due to the presence of coordinated and free P centers in the cyclodiphosphazane ligand. Further, no Ag–P coupling was observed even at −50 °C, which may be due to the fluxional behavior in solution. Similar complexes show both $^1J(^{107}Ag\text{–}P)$ and $(^{109}Ag\text{–}P)$ values on the order of 500–600 Hz.[9] The IR spectrum of the Ag^I polymer **3** shows a strong $\nu(CN)$ band at 2143 cm^{-1} which is at a slightly lower frequency as compared to the same in free AgCN ($\nu(CN) = 2164$ cm^{-1})[10] due to the π-acceptor nature of the cyclodiphosphazane. Complexes **2–4** are sensitive to light and they decompose on exposure to light for a week to give black metallic powder. The molecular structures of **2** and **4** are confirmed by single-crystal X-ray diffraction studies, whereas the proposed structure of **3** is based on NMR spectroscopy, elemental analysis and mass spectrometry.

Molecular structures of 2 and 4

Molecular structures of complexes **2** and **4** with atom numbering schemes are shown in Fig. 1 and 2, respectively. Crystallographic information and the details of the structure determination are summarized in Table 1. The important bond distances and bond angles for **2** and **4** are listed in Tables 2 and 3, respectively.

Crystals of complex **2** were obtained by slow diffusion of Et_2O into the dichloromethane solution of **2** at room temperature. In

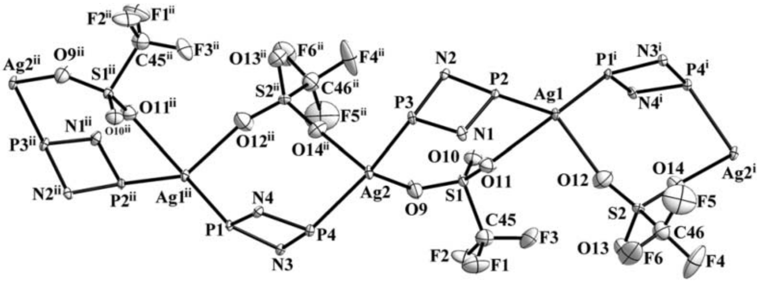

Fig. 1 Section of the polymeric structure of **2**. Thermal ellipsoids are at 50% probability. For clarity all substituents on phosphorus and nitrogen have been omitted. View axes: 90.60X, 35.31Y, 95.23Z. Symmetry operation i = 3/2 − x, 1 − y, 1/2 + z, ii = 3/2 − x, −1 − y, −1/2 + z.

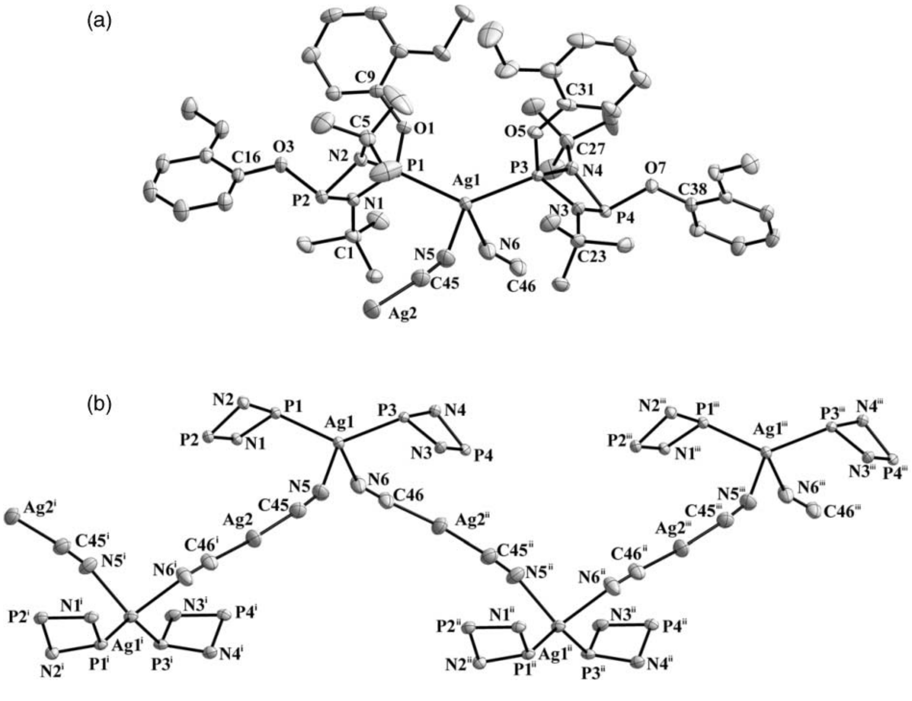

Fig. 2 (a) Structure of the asymmetric unit in **4**. Thermal ellipsoids are at 50% probability. (b) Polymeric structure of **4**. Thermal ellipsoids are at 50% probability. For clarity all substituents on phosphorus and nitrogen have been omitted. View axes: 146.89X, −37.80Y, −110.49Z. Symmetry operation i = 1/2 − x, −1/2 + y, 1/2 − z, ii = 1/2 − x, 1/2 + y, 1/2 − z, iii = 1/2 − x, 3/2 + y, 1/2 − z.

Table 1 Crystal data and details of the structure determination for **2** and **4**

	2	**4**
Formula	$C_{46}H_{64}Ag_2F_6N_4O_{14}P_4S_2$	$C_{46}H_{64}Ag_2N_6O_8P_4$
fw	1414.75	1168.65
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a/Å	14.127(1)	16.482(1)
b/Å	19.570(2)	16.069(1)
c/Å	21.228(2)	22.312(2)
α/°	90	90
β/°	90	105.269(1)
γ/°	90	90
V/Å^3	5869(1)	5700.8(6)
Z	4	8
ρ_{calc}/g cm^{-3}	1.601	1.362
μ(MoKα)/mm^{-1}	0.929	0.849
F(000)	2880	2400
Crystal size/mm^3	0.03 × 0.06 × 0.12	0.19 × 0.21 × 0.26
T/K	100	100
2θ range/deg	1.7–24.8	2.2–28.4
Total no. reflns	23836	99847
No. of indep. reflns [$R_{\mathrm{int}} = 0.036$]	23838	14182
Flack parameter	−0.01(3)	
R_1[a]	0.0805 ($F^2 > 4\sigma(F^2)$)	0.0427 ($F^2 > 4\sigma(F^2)$)
wR_2[b]	0.1520	0.1129
GOF (F^2)	1.09	1.03

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond distances and bond angles for **2**

Bond distances/Å		Bond angles/°	
Ag1–P1	2.430(3)	P1–Ag1–P2	136.85(6)
Ag1–P2	2.447(3)	P1–Ag1–O11	126.15(10)
Ag2–P3	2.437(3)	P1–Ag1–O12	97.81(11)
Ag2–P4	2.442(3)	P2–Ag1–O11	76.90(10)
Ag1–O11	2.596(5)	P2–Ag1–O12	118.72(11)
Ag1–O12	2.390(5)	O11–Ag1–O12	92.98(14)
Ag2–O9	2.390(5)	P3–Ag2–P4	141.09(6)
Ag2–O14	2.546(5)	P3–Ag2–O9	106.75(11)
S1–O9	1.457(5)	P3–Ag2–O14	109.81(10)
S1–O10	1.417(5)	P4–Ag2–O9	108.63(11)
S1–O11	1.428(4)	P4–Ag2–O14	88.56(10)
S1–C45	1.793(8)	O9–Ag2–O14	85.76(14)
S2–O12	1.443(5)	O9–S1–O11	113.6(3)
S2–O13	1.417(5)	O12–S2–O14	114.3(3)
S2–O14	1.431(5)	Ag1–O11–S1	142.8(3)
S2–C46	1.796(9)	Ag1–O12–S2	146.0(3)
P1–N3	1.713(5)	Ag2–O9–S1	130.2(2)
P1–N4	1.692(5)	Ag2–O14–S2	163.7(3)
P2–N1	1.690(6)	P1–N3–P4	96.6(3)
P2–N2	1.692(5)	P1–N4–P4	97.5(2)
P3–N1	1.703(5)	N3–P1–N4	82.1(2)
P3–N2	1.695(6)	N3–P4–N4	83.1(2)
P4–N3	1.687(6)	P2–N1–P3	96.7(3)
P4–N4	1.686(5)	P2–N2–P3	96.9(3)

Table 3 Selected bond distances and bond angles for **4**

Bond distances/Å		Bond angles/°	
Ag1–P1	2.418(1)	P1–Ag1–P3	134.06(2)
Ag1–P3	2.423(1)	P1–Ag1–N5	101.09(7)
Ag1–N5	2.301(3)	P3–Ag1–N6	95.35(7)
Ag1–N6	2.340(3)	N5–Ag1–N6	96.03(11)
N5–C45	1.129(5)	Ag1–N5–C45	152.0(3)
Ag2–C45	2.042(3)	N5–C45–Ag2	174.8(3)
Ag2–C46	2.054(3)	C45–Ag2–C46	173.86(13)
C46–N6	1.124(4)	Ag2–C46$^{\mathrm{i}}$–N6$^{\mathrm{i}}$	79.67(12)
P1–N1	1.693(2)	P1–N1–P2	96.92(11)
P1–N2	1.682(2)	P1–N2–P2	97.20(11)
P2–N1	1.709(2)	N1–P1–N2	82.46(11)
P2–N2	1.712(2)	N1–P2–N2	81.12(11)
P3–N3	1.689(2)	P3–N3–P4	96.30(13)
P3–N4	1.687(2)	P3–N4–P4	98.70(12)
P4–N3	1.754(3)	N3–P3–N4	81.75(11)
P4–N4	1.694(2)	N3–P4–N4	79.67(12)

complex **2**, cyclodiphosphazane and trifluoromethanesulfonate (OTf) ligands are bridging the two different silver(I) atoms to give a chain-like 1-D polymeric structure as shown in Fig. 1. Each repeat unit consists of two silver atoms bridged by cyclodiphosphazane and OTf (O,O) ligands to form a chain of eight-membered rings in a spirocyclic fashion.

The possible coordination modes for tri- and tetradentate Ag$^{\mathrm{I}}$ polymers containing both bisphosphines and anionic ligands are shown in Chart 1.[11] Interestingly, the coordination polymers of the type **V** (complex **2**) containing two Ag$^{\mathrm{I}}$ ions bridged by both the bisphosphines and anionic ligands are not known, whereas the other structures of the type **I**–**IV** are routinely observed. In the case of **2**, the cyclodiphosphazane (**1**) and the triflate anions form eight-membered rings [Ag(X-κO,κO)(**1**-κP,κP)Ag], which are connected linearly to give a polymeric structure (**2**). The majority of tetra-coordinated silver(I) polymers consist of two different cyclic building blocks ([Ag(X-κO,κO)$_2$Ag] and [Ag(P–P-κP,κP)$_2$Ag]), which are arranged alternate to give polymeric complexes of the type **I**–**IV**. The silver(I) centers present in **2** are four-coordinated (AgP_2O_2) with distorted tetrahedral geometry. The tetrahedral angles vary from 136.85(6)° to 76.90(10)° at the Ag1 center, whereas at the Ag2 center the angles vary from 141.09(6)° to 85.76(14)°. The distortions in the coordination geometries around Ag1 and Ag2 decrease the strain created during

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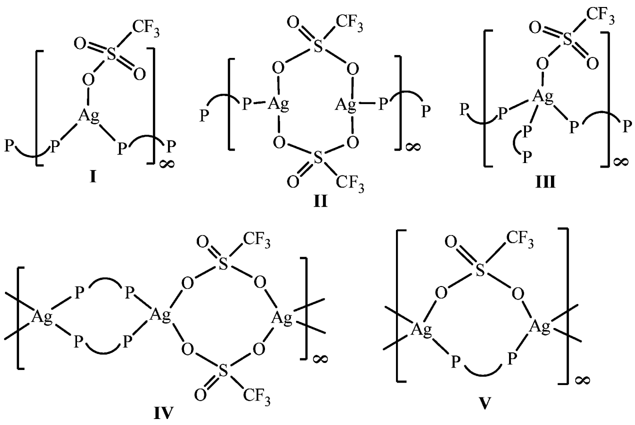

Chart 1 Possible coordination modes for Ag polymers.

the formation of one dimensional polymer **2**. The distance between Ag1 and Ag2 is 5.723 Å which is too long for any Ag···Ag bonding interactions.[12] This is as expected since the rigidity of the cyclodiphosphazane ligand enforces a relatively large metal–metal separation when it functions as a bridging ligand. The normal span of the triflate ligand when functioning in an *O*,*O*′-bridging mode is less. Consequently it adopts an asymmetrical bridging mode here presumably so as to form one relatively strong bond to silver. The exocyclic phenyl substituents on phosphorus are arranged in *endo*,*exo* fashion.

The X-ray quality single crystals of **4** were grown from CH_3CN–THF (1 : 1) solution at −30 °C. The molecular structure of **4** consists of $[(P_2N_2)_2Ag]^+$ moieties linked by $[NCAgCN]^-$ bridging unit in an alternating zig-zag fashion to form a one-dimensional Ag^I coordination polymer (Fig. 2). The approximate distances between the Ag1···Ag1 and Ag1···Ag1^i atoms are 16.069 Å and 10.087 Å, respectively. Two different Ag^I cations with different coordination numbers are present in molecule **4**. The Ag1 center adopts a distorted tetrahedral geometry being coordinated by a phosphorus atom from each of two different cyclodiphosphazane ligands and a nitrogen atom from each of two cyanide units. The angles at silver vary from 134.06(2)° to 95.35(7)°. The Ag2 center is di-coordinated being bound to the carbon atoms of the two bridging cyanide groups with a C45–Ag2–C46 angle of 173.86(13)°. In a previously reported[13] polymeric silver(I) complex, $[(Cy_3P)Ag(NCAgCN)]_\infty$, the terminal silver center is tri-coordinated whereas the corresponding Ag1 center in **4** is tetra-coordinated which may be due to the less bulky nature of the cyclodiphosphazane as compared to PCy_3. The Ag1–P1 and P2–Ag1 bond distances are 2.418(1) Å and 2.423(1) Å, respectively, and are comparable with literature values.[14] The cyclodiphosphazane ligands in complex **4** show *cis* (*endo*,*exo*) confirmation with slightly puckered P_2N_2 rings, as indicated by the sum of the angles around the N center of the cyclodiphosphazane (~355°).

Conclusions

In summary, we describe the synthesis and structures of two novel Ag^I one-dimensional coordination polymers of cyclodiphosphazane. The bridging coordination mode of the rigid P_2N_2 ring favors the linear propagation of a polymeric chain whereas the monodentate mode produces a zig-zag polymeric chain. In the formation of the AgCN polymer, the cyclodiphosphazane ligands play an ancillary role to stabilize the cyanometallated linkers. The structure of [Ag{μ-OTf-κ*O*,κ*O*}{μ-(*o*-$MeOC_6H_4O$)P(μ-N^{t}Bu)-κ*P*,κ*P*}$_2$]$_\infty$ (**2**) is a rare example of both phosphines and anions bridging the two silver atoms simultaneously to form the spirocyclic chains. Presently, we are investigating the coordination behavior of cyclodiphosphazanes with various gold(I) derivatives.

Experimental

General

All manipulations were performed under rigorously anaerobic conditions using high vacuum manifolds and Schlenk techniques. All the solvents were purified by conventional procedures and freshly distilled and degassed prior to use.[15] The compound *cis*-{(*o*-$MeOC_6H_4O$)P(μ-N^{t}Bu)}$_2$ (**1**) was prepared according to the published procedure.[6] AgOTf and AgCN were purchased from commercial sources and used as received. The ^1H and $^{31}P\{^1H\}$ NMR (*δ* in ppm) spectra were recorded using a Varian Mercury Plus spectrometer operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. IR spectra were recorded on a Nicolet Impact 400 FT-IR instrument in KBr disks. Microanalyses were performed on a Carlo Erba Model 1112 elemental analyzer. Mass spectrometry experiments were carried out using a Waters Q-Tof micro-YA-105. Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of [Ag{μ-OTf-κ*O*,κ*O*}{μ-(*o*-$MeOC_6H_4O$)P(μ-N^{t}Bu)-κ*P*,κ*P*}$_2$]$_\infty$ (2). A dichloromethane solution (15 cm^3) of *cis*-{(*o*-$MeOC_6H_4O$)P(μ-N^{t}Bu)}$_2$ (**1**) (114 mg, 0.25 mmol) was added dropwise to a AgOTf (65.1 mg, 0.25 mmol) suspension in dichloromethane (5 cm^3) at room temperature. The colorless reaction mixture was stirred further for 6 h with minimum light exposure. The volume of the solution was reduced to 7 cm^3, diluted with 3 cm^3 of diethyl ether and stored at −30 °C for a day to give a white crystalline solid (130 mg, 73%). Mp 124–126 °C (decomp.). $C_{23}H_{32}N_2O_7F_3P_2SAg$ (707.4): calcd C 39.05, H 4.55, N 3.96, S 4.53; found: C 39.17, H 4.82, N 3.76, S 4.69%. IR (KBr disk, cm^{-1}): 1499 (s), 1456 (s), 1370 (m), 1256 (s), 1168 (s), 1028 (s), 893 (s). ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.32$–6.86 (m, 8 H, Ph), 3.84 (s, 6 H, OMe), 1.41 (s, 18 H, ^{t}Bu) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta_P = 116.6$ (br s) ppm.

Synthesis of [Ag{OTf-κ*O*,κ*O*}({(*o*-$MeOC_6H_4O$)P(μ-N^{t}Bu)-κ*P*}$_2$)$_2$] (3). A dichloromethane (15 cm^3) solution of *cis*-{(*o*-$MeOC_6H_4O$)P(μ-N^{t}Bu)}$_2$ (**1**) (151 mg, 0.34 mmol) (7 cm^3) was added dropwise over a dichloromethane suspension of AgOTf (43.2 mg, 0.17 mmol) at room temperature. The reaction mixture was stirred for 4 h, concentrated to 10 cm^3, diluted with 5 cm^3 of diethyl ether and stored at −30 °C for a day to afford product as a white crystalline solid (167 mg, 86%). Mp 146–148 °C. $C_{45}H_{64}N_4O_{11}F_3P_4SAg$ (1157.8): calcd C 46.68, H 5.57, N 4.83, S 2.76; found: C 46.92, H 5.63, N 5.03, S 2.87%. IR (KBr disk, cm^{-1}): 1497 (vs), 1458(w), 1256 (s), 1201 (m), 1111 (m), 1026 (s), 905 (s). ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.30$–6.85 (m, 16 H, Ph), 3.84 (s, 12 H, OMe), 1.42 (s, 36 H, ^{t}Bu) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): $\delta_P = 139.9$ (br s), 112.8 (br s) ppm. MS(EI): *m*/*z* 1009.00 (M − OTf).

Synthesis of [Ag{NCAgCN}({(*o*-MeOC$_6$H$_4$O)P(μ-N^{t}Bu)-κ*P*}$_2$)$_2$]$_\infty$ (4). A mixture of **1** (196 mg, 0.44 mmol) and AgCN (58.4 mg, 0.44 mmol) in acetonitrile (25 cm^3) was stirred under reflux conditions for 6 h. The reaction mixture was cooled to room temperature, concentrated to 10 cm^3 under reduced pressure and stored at −30 °C for a day to give a white crystalline product (226 mg, 89%). Mp 110–112 °C. $C_{23}H_{32}N_3O_4P_2Ag$ (584.3): calcd C 47.27, H 5.51, N 7.19; found: C 47.32, H 5.47, N 7.47%. IR (KBr disk, cm^{-1}): 2143 [ν(C≡N)]. ^{1}H NMR (400 MHz, acetone-d$_6$): $\delta_H = 7.35–6.89$ (m, 8 H, Ph), 3.86 (s, 6 H, OMe), 1.44 (s, 18 H, ^{t}Bu) ppm. ^{31}P{^{1}H} NMR (161 MHz, acetone-d$_6$): $\delta_P = 137.2$ (br s) ppm.

X-Ray crystallography

Crystals of **2** and **4** were mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex low temperature attachment of a Bruker Smart APEX CCD diffractometer. Full spheres of intensity data were collected as follows: for **2**, three sets of 400 scans in ω (0.5° per scan at $\varphi = 0$, 90 and 180°) and two sets of 800 scans in φ (0.45° per scan at $\omega = -30$ and 210°); for **4**, three sets of 606 scans in ω (0.3° per scan at $\varphi = 0$, 120 and 240°). Intensity data were collected using the SMART software package[16] and these were reduced to F^2 values with the SAINT+ software[17] which also performed a global refinement of unit cell parameters using 7372 (for **2**) and 8660 (for **4**) reflections chosen from the full data set. The crystal of **2** proved to be twinned and the integration of the raw data was carried out with the two-component version of SAINT+ using the two-component orientation file prepared by CELL_NOW[18] and with the cell parameters of the second domain on the twin constrained to be identical to those of the first domain. Multiple measurements of equivalent reflections provided a basis for empirical absorption corrections (using the programs TWINABS[19] for **2** and SADABS[20] for **4**. In the case of **2**, the corrected F^2 data were merged according to the point group 222 but with the exclusion of those reflections for which one or more of the symmetry equivalents was a composite. The structures were solved by direct methods and refined by full-matrix, least-squares procedures using the SHELXTL program suite.[21] For **2**, the small size of the crystal resulted in there being little useful diffraction data beyond $2\theta = 49.2°$ so with a limited amount of high order data it was not feasible to carry out a refinement of the light atoms with unrestricted anisotropic displacement parameters. Instead, they were restrained to approximate isotropic behavior. In the case of **4**, two of the *tert*-butyl groups are rotationally disordered over two resolved sites while one of the P–O–R groups is also disordered. All three disordered groups were refined subject to restraints that they approximate idealized geometries. Details of the disorder are provided in the CIF. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å (aromatic rings) and 0.98 Å (methyl groups)) and included as riding contributions with isotropic displacement parameters 1.2 (aromatic) or 1.5 (methyl) times those of the attached carbon atoms.

CCDC reference numbers 641238 (**2**) and 641239 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704303a

Acknowledgements

We are grateful to the Department of Science and Technology (DST), New Delhi for funding through grant SR/S1/IC-05/2003. PC thanks CSIR for Research Fellowship. JTM thanks the Louisiana Board of Regents through grant LEQSF(2002-03)-ENH-TR-67 for purchase of the Bruker APEX CCD diffractometer and the Chemistry Department of Tulane University for support of the X-ray laboratory.

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