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Tris(4-methylpiperazin-1-yl)phosphane, $P(NC_4H_8NMe)_3$: Synthesis, Structural Studies, Group 10 and 11 Metal Complexes and Catalytic Investigations

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Group 10 and 11 metal complexes of a multidentate phosphorus–nitrogen donor ligand tris(4-methylpiperazin-1-yl)-phosphane, $P(NC_4H_8NMe)_3$ (**1**) are reported. The reactions of **1** with an equimolar amount of CuX (X = Cl, Br and I) afford tetranuclear cubane-like complexes $[(CuX)\{P(NC_4H_8NMe)_3\}]_4$ (**2**, X = Cl; **3**, X = Br and **4**, X = I) in excellent yield. Treatment of **1** with $AuCl(SMe_2)$ produces a mononuclear complex, $[(AuCl)\{P(NC_4H_8NMe)_3\}]$ (**5**). Reaction of **1** with AgCN produces a 2D Ag^I polymeric sheet, $[(AgCN)_2\{P(NC_4H_8NMe)_3\}]_n$ (**6**) in moderate yield. The similar 1:1 reactions of **1** with AgX (X = Cl and Br) furnish dinuclear complexes, $[(AgX)\{P(NC_4H_8NMe)_3\}]_2$ (**7**, X = Cl and **8**, X = Br). The 2:1 reactions of **1** with $[M(COD)Cl_2]$ (M = Pd or Pt) afford $[\{P(NC_4H_8NMe)_3\}_2MCl_2]$ (**9**, M = Pd and **10**, M = Pt) in quantitative yield. The molecular structures of complexes **1**–**3** and **6** are established through single-crystal X-ray diffraction studies. The catalytic activity of the Pd^{II} complex **9** has been investigated in Suzuki cross coupling reactions.

Introduction

In recent years there has been a growing interest in the synthesis of complex structures including polymers, 2D sheets, helices and cage complexes through the use of dynamic coordination chemistry[1] and weak intermolecular forces such as hydrogen bonding, π-stacking, dipole-dipole attractions and van der Waals interactions.[2] The motivation behind such investigations is to produce molecules with intriguing architectures and topologies, and with properties for producing functional solid materials for catalysis and optical and magnetic applications.[3] Multidentate ligands containing both hard and soft donor atoms with Group 11 metal derivatives have been used widely in this field.[4] Other than the coordinative interaction afforded by these multidentate ligands, the metals often show weak bonding interactions between the closed-shell metal centers to produce novel molecular architectures with exciting optical properties.[5] The nature of this d^{10}/d^{10} interaction has been of particular interest to theoreticians and spectroscopists for a long time.[6] The nature of the product formed depends on the arrangement of rhombic M_2X_2 units that can be not only simple dimers,[7] but also cubane-like[8] or step structures.[9] It would be interesting to study interactions of Group 11 halides with phosphanes containing additional donor functionalities, which may produce more coordinative interactions to give interesting structures with extended networks. As a part of our interest in designing new ligands and studying their coordination behavior and catalytic applications,[10] we report herein the synthesis, coordination chemistry and catalytic investigations of tris(4-methylpiperazin-1-yl)phosphane, $P(NC_4H_8NMe)_3$ (**1**).

Results and Discussion

The reaction of phosphorus trichloride with six equivalents of *N*-methylpiperazine afforded a mixed donor multidentate ligand tris(4-methylpiperazin-1-yl)phosphane, $P(NC_4H_8NMe)_3$ (**1**) in good yield.[11] Compound **1** is a white crystalline solid that readily absorbs moisture from the atmosphere to become deliquescent. The crude product can be purified easily by dissolving it in petroleum ether and filtering to remove impurities. Treatment of **1** with CuX (X = Cl, Br and I) in an equimolar ratios produces tetranuclear complexes, $[(CuX)\{P(NC_4H_8NMe)_3\}]_4$ (**2**, X = Cl; **3**, X = Br; **4**, X = I) in quantitative yields, as shown in Scheme 1. Complexes **2** and **3** are pale green solids, whereas complex **4** is a white crystalline solid. A similar reaction with $AuCl(SMe_2)$ in a 1:1 molar ratio afforded a mononuclear complex, $[(AuCl)\{P(NC_4H_8NMe)_3\}]$ (**5**). The ^{31}P NMR spectra of complexes **2**–**5** show single resonances at 98.9, 92.7, 79.5 and 102.3 ppm, respectively, which are shielded compared to the free ligand **1** (δ = 112.2 ppm). In the ^1H NMR spectra of complexes **2**–**5**, the peak corresponding to the *N*-methyl protons appears as a singlet in the region 2.24–2.30 ppm, whereas the –NMeCH_2 and –NCH_2 pro-

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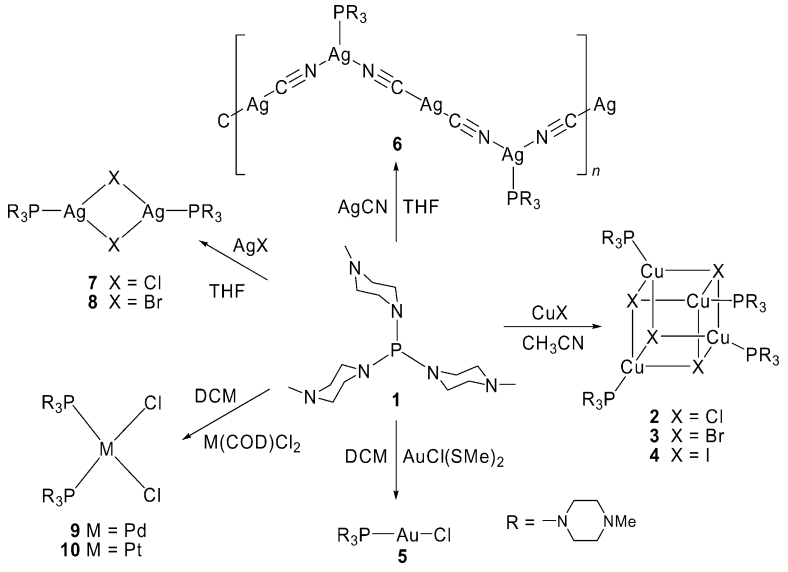

Scheme 1.

tons appear as broad singlets in the regions 2.33–2.36 and 3.10–3.17 ppm, respectively. The spectral and analytical data support the proposal that **2**–**5** form only monoligated complexes, and the structures of **1**–**3** were confirmed by single crystal X-ray diffraction studies.

The reaction of **1** with AgCN is not dependent on the stoichiometry of the reagents or the reaction conditions, and affords a 2D zigzag polymeric sheet, $[(AgCN)_2\{P(NC_4H_8NMe)_3\}]_n$ (**6**) in moderate yield. The equimolar reactions of **1** with AgX (X = Cl or Br) afford halo-bridged dinuclear complexes, $[(AgX)\{P(NC_4H_8NMe)_3\}]_2$ (**7**, X = Cl; **8**, X = Br) in good yield. The ^{31}P NMR spectrum of complex **6** shows a broad doublet centered at δ = 108.8 ppm with a $^1J_{AgP}$ coupling of 717 Hz, whereas complexes **7** and **8** show two doublets centered at δ = 111.4 and 108.7 ppm, respectively, with $^1J^{109}{}_{AgP}$ and $^1J^{107}{}_{AgP}$ couplings of 929 and 804 Hz and of 854 and 743 Hz, respectively. The $^1J_{AgP}$ values for complexes **6**–**8** follow the order Cl > Br > CN, which was also observed for $(t\text{Bu})_3\text{PAgX}$ (X = Cl, Br, CN)[12] and $[Cy_3PAgX]_2$ (X = Cl, Br).[13] The 2:1 reactions of **1** with $[M(COD)Cl_2]$ (M = Pd or Pt) afford $[\{P(NC_4H_8NMe)_3\}_2MCl_2]$ (**9**, M = Pd; **10**, M = Pt) in quantitative yield. The ^{31}P NMR spectra of complexes **9** and **10** consist of single resonances at δ = 89.5 and 84.4 ppm, respectively, in which the platinum bound phosphorus center of **10** exhibits ^{195}Pt satellites with a $^1J_{Pt-P}$ coupling of 3236 Hz. The ^1H NMR spectroscopic data for complexes **6**–**10** are consistent with the proposed structures (Table 1). The IR spectrum of complex **6** shows a strong ν(CN) band at 2140 cm^{-1}, which is at a slightly lower frequency when compared to the same band in the spectrum of free AgCN [ν(CN) = 2164 cm^{-1}].[14] The spectral and analytical data support the proposed structures for complexes **6**–**10**, and the structure of complex **6** was confirmed by a single crystal X-ray diffraction study.

Table 1. NMR spectroscopic data for compounds **1**–**10**.

	^{31}P NMR (δ, ppm)	$^1J_{XP}$ / Hz (X = Ag or Pt)	^1H NMR (δ, ppm) –N*Me*	MeNC*H*$_2$–	–NC*H*$_2$–
1	112.2 (s)		2.27 (s)	2.32 (br. s)	2.94 (br. s)
2	98.9 (s)		2.27 (s)	2.36 (br. s)	3.10 (br. s)
3	92.7 (br. s)		2.25 (s)	2.35 (br. s)	3.12 (br. s)
4	79.5 (br. s)		2.24 (s)	2.33 (br. s)	3.17 (br. s)
5	102.3 (s)		2.22 (s)	2.30 (br. s)	3.15 (br. s)
6	108.8 (d)	717	2.30 (s)	2.37 (br. s)	3.03 (br. s)
7	111.4 (2 d)	929, 804	2.29 (s)	2.38 (br. s)	3.09 (br. s)
8	108.7 (2 d)	854, 743	2.25 (s)	2.35 (br. s)	3.09 (br. s)
9	89.5 (s)		2.23 (s)	2.37 (br. s)	3.22 (br. s)
10	84.4 (s)	3236	2.28 (s)	2.41 (br. s)	3.27 (br. s)

The Crystal and Molecular Structures of 1–3 and 6

Views of the molecular structures of compounds **1**–**3** and **6** with atom numbering schemes are shown in Figures 1, 2,

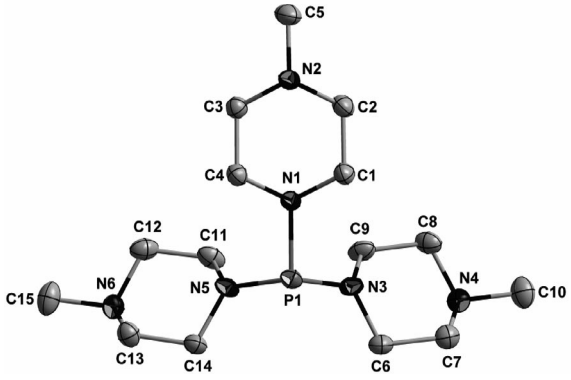

Figure 1. Molecular structure of **1**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

and 3. Crystal data and details of the structure determinations are given in Table 5, while selected bond lengths and bond angles are given in Tables 2 and 3.

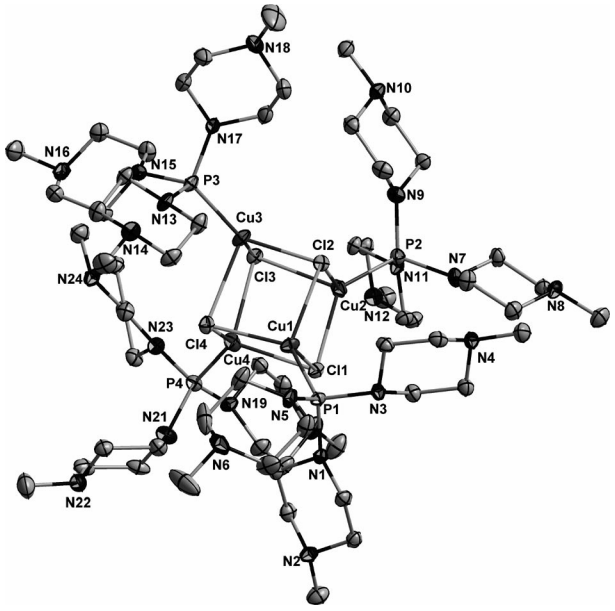

Figure 2. Molecular structure of **2**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

The molecule **1** crystallizes in the triclinic crystal system with space group $P\bar{1}$ (No.2). There are two short, P1–N3 and P1–N5, and one long, P1–N1, phosphorus–nitrogen bonds with distances of 1.693(1), 1.691(2) and 1.741(2) Å, respectively. The *N*-methylpiperazine groups, which are linked through short bonds to the phosphorus atom, are twisted in opposite directions, this was also observed in analogous tertiary aminophosphanes.[15] The N1–P1–N3 and N1–P1–N5 angles [97.29(7)° and 97.18(7)°] are smaller than the N3–P1–N5 angle [110.56(7)°], and the sum of the angles around phosphorus atom is 305.03°.

The molecular structure of **2** consists of a distorted cubane-like $P_4Cu_4Cl_4$ framework, with alternating corners of the cube being occupied by copper and chlorine atoms, and with each phosphorus atom projecting radially from a copper atom. The Cu–P bond lengths are equal within experimental error with an average of 2.174(1) Å, which is comparable to the distance found in the PEt_3 analog [2.176(1) Å].[8a] The Cu–Cl bond lengths vary from 2.321(1) to 2.602(1) Å. The six Cu···Cu bond lengths, in increasing order, are 3.092, 3.238, 3.323, 3.354, 3.377 and 3.384 Å, which are longer than those found in the Cu_4Cl_4 cube that has bridged-bidentate phosphaalkene ligands (3.058–3.218 Å).[16] The Cl–Cu–Cl angles range from 88.74(2) to 101.09(2)°, whereas the Cu–Cl–Cu angles are smaller and range from 78.05(2) to 89.05(2)°.

Complex **3** is isomorphous and isostructural with **2** and has a similar $P_4Cu_4Br_4$ cubane core. The bond lengths and bond angles in **3** are similar to those in **2**.

The molecular structure of **6** consists of $[\{P(NC_4H_8NMe)_3\}Ag]^+$ moieties bridged by $[NCAgCN]^-$ units in an alternating zigzag fashion to form an Ag^I polymeric chain. These chains are stacked one over the other, with a weak nitrogen coordinative interaction between the *N*-methylpiperazine moiety and Ag2 [Ag2–N6, 2.605(2) Å], to yield a 2D Ag^I sheet. The Ag···N interactions observed are nontrivial and are 0.03 Å shorter than those found in the $AgC(CN)_3$ based coordination polymer Ag(tcm)(bpe) [tcm = tricyanomethanide, bpe = 1,2-bis(4-pyridyl)ethane].[1d] In **6**, Ag1 has trigonal planar geometry being bonded to the nitrogen atoms of two linear $[NCAgCN]^-$ bridges and a phosphorus atom of **1**. The angles about Ag1, P–Ag1–N7, P–Ag1–N8 and N7–Ag1–N8, are 126.15(5), 133.31(6) and 100.48(8)°, respectively, with the sum of these angles being close to 360°. The Ag2 center adopts a T-shape coordination geometry that consists of the carbon atoms of the two bridging cyanide groups and a nitrogen atom of the *N*-methylpiperazine group, with the C16–Ag2–C17, N6–Ag2–C16, N6–Ag2–C17 angles being 160.53(9), 104.96(8) and 94.24(7)°, respectively. The Ag1–P, Ag1–N7 and Ag1–N8 bond lengths are 2.355(1), 2.233(2) and 2.173(2) Å, respectively. These values are significantly shorter than the corresponding values found for the analogous 1D polymers of $P(Cy)_3$[14], and the functionalized cyclodiphosphazane *cis*-$\{(o\text{-}MeOC_6H_4O)P(\mu\text{-}NtBu)\}_2$.[17] The Ag2–C16 and Ag2–C17 bond lengths are 2.068(2) and 2.079(2) Å, respectively, and are 0.03 Å longer than the corresponding distances observed in the above mentioned polymers.

Suzuki–Miyaura Cross-Coupling Reactions

The palladium catalyzed Suzuki cross-coupling reaction is one of the efficient methods for forming symmetric and nonsymmetric biaryl compounds in organic synthesis.[18] Complex **9** proved to be an efficient catalyst for the Suzuki–Miyaura cross-coupling reactions of aryl bromides with phenylboronic acid, and led to good conversions with low catalytic loadings. The Suzuki–Miyaura cross-coupling reactions were carried out in methanol (5 mL) with potassium carbonate as base. For example, bromo- or iodobenzene and phenylboronic acid in the presence of K_2CO_3 in methanol gives 95% conversion within 4–5 h, at room temperature with 0.05 mol-% of catalyst (Table 4, entries 1 and 2). Higher conversion rates were realized when activated aryl bromides were used as substrates (Table 4, entries 3, 5 and 8). The coupling of 4-bromoacetophenone with phenylboronic acid afforded 75% of the coupled product within half an hour (turn over frequency: 3000) and complete conversion was achieved after 4 h at room temperature. Even though good conversion was observed with deactivated 4-bromoanisole (Table 4, entry 4) very low catalytic conversion was observed with 1-bromo-2,4-dimethoxybenzene (Table 4, entry 11). The coupling reactions of bulky aryl bromides with phenylboronic acid tend to give moderate yield at room temperature (Table 4, entry 9), however the conversion rate and yield can be improved by carrying out the reaction under reflux conditions (Table 4, entry 10). Coupling reactions performed with 1,3-dibromobenzene

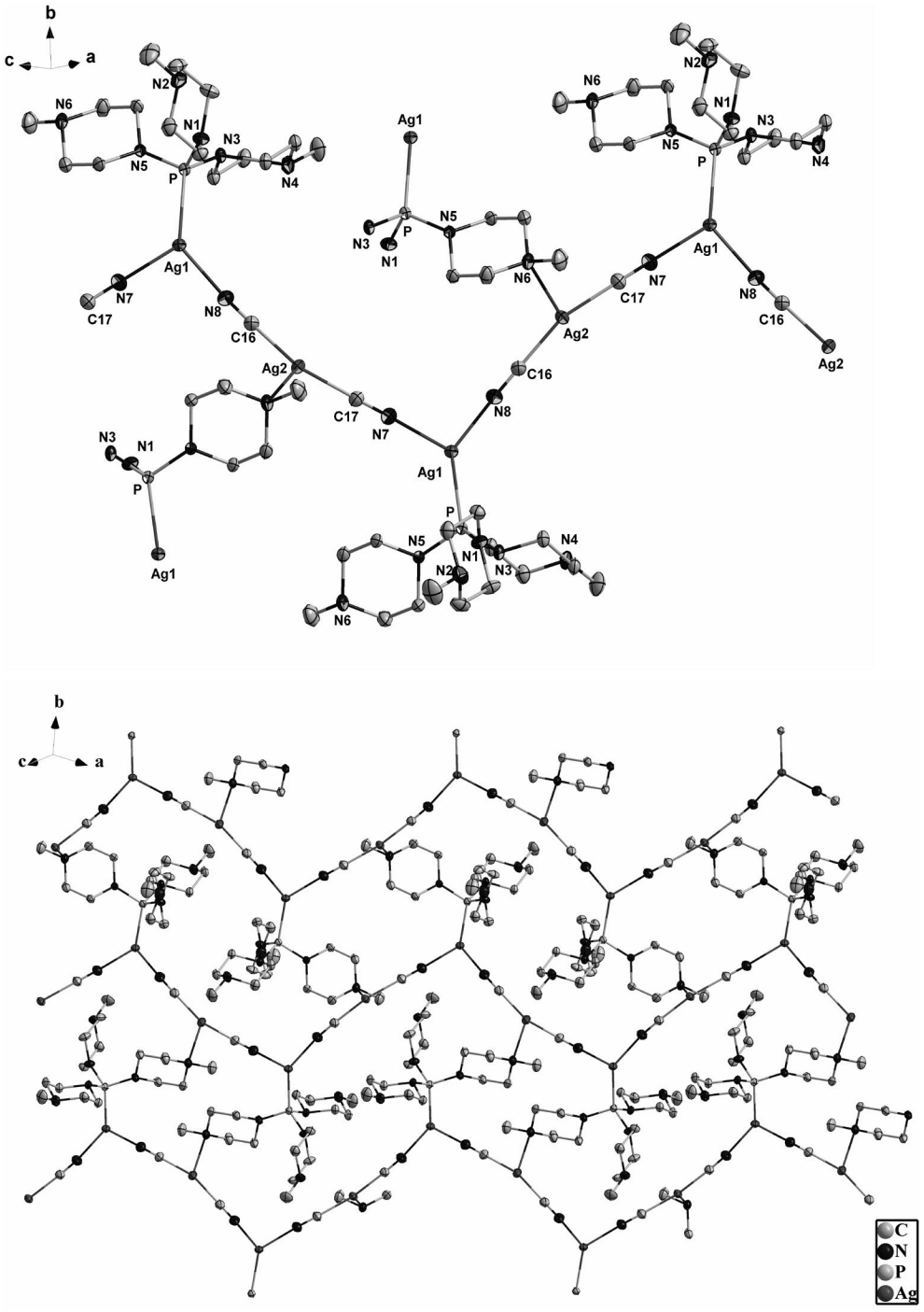

Figure 3. (top) A portion of the zigzag chain present in the structure of **6**. Symmetry operations: (i) –1 + *x*, *y*, 1 + *z*; (ii) 0.5 – *x*, 0.5 + *y*, 0.5 – *z*; (iii) 0.5 – *x*, 0.5 + *y*, –0.5 – *z*; (iv) –1 + *x*, –1 + *y*, 1 + *z*. (bottom) A portion of the 2-D sheet present in the structure of **6**. All hydrogen atoms have been omitted for clarity, and displacement ellipsoids are drawn at the 50% probability level in both diagrams.

yielded 83% of 1,1′:3′,1"-terphenyl and 17% of 3-bromobiphenyl after 2 h with the complete consumption of the 1,3-dibromobenzene reagent. A gradual increase in the yield of 1,1′:3′,1"-terphenyl was observed with time and a maximum of 98% conversion to 1,1′:3′,1′′-terphenyl was achieved after 24 h (Table 4, entry 13). Similarly 1,4-dibromobenzene yielded 86% of 1,1′:4′,1′′-terphenyl and 12% of 4-bromobiphenyl after 3 h however, a small amount of unreacted 1,4-dibromobenzene (2%) remained. All the 1,4-dibromobenzene was consumed within 5 h and a conversion of $<$97% of 1,1′:4′,1′′-terphenyl was achieved within 24 h (Table 4, entry 14). Similarly, the coupling reactions performed with 9, 10-dibromoanthracene and 1, 3, 5-tribromobenzene with phenylboronic acid yielded 100% of di- and tri-substituted derivatives, respectively (Table 4, entries 15 and 16), whereas 4,4′-dibromobiphenyl afforded 83% of di-

Table 2. Selected bond lengths and bond angles for compounds **1** and **2**.

Compound **1** Bond lengths / Å		Bond angles / °		Compound **2** Bond lengths / Å		Bond angles / °	
P1–N1	1.741(2)	N1–P1–N3	97.29(7)	Cu1–P1	2.1739(5)	Cl1–Cu1–Cl2	92.40(2)
P1–N3	1.693(1)	N1–P1–N5	97.18(7)	Cu2–P2	2.1740(6)	Cl1–Cu1–Cl4	99.08(2)
P1–N5	1.691(2)	N3–P1–N5	110.56(7)	Cu3–P3	2.1756(5)	Cl2–Cu1–Cl4	95.55(2)
N1–C1	1.476(2)	P1–N1–C1	114.66(1)	Cu4–P4	2.1732(6)	Cl1–Cu2–Cl2	94.18(2)
N1–C4	1.470(2)	P1–N1–C4	114.38(1)	Cu1–Cl1	2.4882(6)	Cl1–Cu2–Cl3	97.23(2)
N3–C6	1.456(2)	P1–N3–C6	118.61(1)	Cu1–Cl2	2.3978(6)	Cl2–Cu2–Cl3	88.74(2)
N3–C9	1.464(2)	P1–N3–C9	125.07(1)	Cu1–Cl4	2.3701(6)	Cl2–Cu3–Cl3	95.75(2)
N5–C11	1.463(2)	P1–N5–C11	126.40(1)	Cu2–Cl1	2.3212(6)	Cl2–Cu3–Cl4	90.02(2)
N5–C14	1.461(2)	P1–N5–C14	117.10(1)	Cu2–Cl2	2.4919(6)	Cl3–Cu3–Cl4	94.20(2)
				Cu2–Cl3	2.5234(6)	Cl1–Cu4–Cl3	95.62(2)
				Cu3–Cl2	2.3860(6)	Cl1–Cu4–Cl4	101.09(2)
				Cu3–Cl3	2.3425(6)	Cl3–Cu4–Cl4	96.64(2)
				Cu3–Cl4	2.6020(6)	Cl1–Cu1–P1	109.08(2)
				Cu4–Cl1	2.4215(6)	Cl1–Cu2–P2	130.82(2)
				Cu4–Cl3	2.4874(6)	Cl2–Cu3–P3	130.23(2)
				Cu4–Cl4	2.3668(6)	Cl1–Cu4–P4	113.70(2)

Table 3. Selected bond lengths and bond angles for compounds **3** and **6**.

Compound **3** Bond lengths / Å		Bond angles / °		Compound **6** Bond lengths / Å		Bond angles / °	
Cu1–P1	2.1886(6)	Br1–Cu1–Br3	93.70(1)	Ag1–P	2.355(1)	P–Ag1–N7	126.15(5)
Cu2–P2	2.1918(6)	Br1–Cu1–Br4	96.26(1)	Ag1–N7	2.233(2)	P–Ag1–N8	133.31(6)
Cu3–P3	2.1880(5)	Br3–Cu1–Br4	101.42(1)	Ag1–N8	2.173(2)	N7–Ag1–N8	100.48(8)
Cu4–P4	2.1939(6)	Br1–Cu2–Br2	97.25(1)	Ag2–N6	2.605(2)	N6–Ag2–C16	104.96(8)
Br1–Cu1	2.5889(4)	Br1–Cu2–Br4	93.85(1)	Ag2–C16	2.068(2)	C16–Ag2–C17	160.53(9)
Br1–Cu2	2.5392(4)	Br2–Cu2–Br4	103.26(1)	Ag2–C17	2.079(2)	N6–Ag2–C17	94.24(7)
Br1–Cu3	2.4946(4)	Br1–Cu3–Br2	92.55(1)	P–N1	1.654(2)	Ag1–P–N1	113.34(7)
Br2–Cu2	2.4849(4)	Br1–Cu3–Br3	99.47(1)	P–N3	1.700(2)	Ag1–P–N3	116.85(6)
Br2–Cu3	2.7184(4)	Br2–Cu3–Br3	97.24(1)	P–N5	1.672(2)	Ag1–P–N5	111.87(6)
Br2–Cu4	2.5013(4)	Br2–Cu4–Br3	99.44(1)	N7–C17	1.146(3)	N1–P–N3	100.87(9)
Br3–Cu1	2.6036(4)	Br2–Cu4–Br4	104.91(1)	N8–C16	1.143(3)		
Br3–Cu3	2.4697(4)	Br3–Cu4–Br4	99.34(1)				
Br3–Cu4	2.6053(4)	Br1–Cu1–P1	121.51(2)				
Br4–Cu1	2.4537(4)	Br1–Cu2–P2	120.73(2)				
Br4–Cu2	2.6029(4)	Br1–Cu3–P3	128.38(2)				
Br4–Cu4	2.5302(4)	Br2–Cu4–P4	125.48(2)				

Table 4. Details of Suzuki cross-coupling reactions for aryl bromides with phenylboronic acid catalyzed by [{$P(NC_4H_8NMe)_3$}$_2PdCl_2$] (**9**).

Entry	Aryl bromide	Condition[a]	% Conversion[b]	TOF[c]	TON[d]
1	bromobenzene	0.05 mol-%, room temp., 4 h	95	475	1900
2	iodobenzene	0.05 mol-%, room temp., 5 h	96	384	1920
3	4-bromoacetophenone	0.05 mol-%, room temp., 1 h	>99	1980	1980
4	4-bromoanisole	0.05 mol-%, room temp., 6 h	99	330	1980
5	4-bromobenzaldehyde	0.05 mol-%, room temp., 4 h	81	405	1620
6	3-bromobenzaldehyde	0.05 mol-%, room temp., 12 h	55	92	1100
7	3-bromobenzaldehyde	0.05 mol-%, reflux, 4 h	99	495	1980
8	4-bromobenzonitrile	0.05 mol-%, room temp., 4 h	97	485	1940
9	2-bromo-6-methoxynaphthalene	0.05 mol-%, room temp., 24 h	64	53	1280
10	2-bromo-6-methoxynaphthalene	0.05 mol-%, reflux, 3 h	97	647	1940
11	1-bromo-2,4-dimethoxybenzene	0.05 mol-%, reflux, 2 h	32	320	640
12	2-bromopyridine	0.05 mol-%, room temp., 6 h	35	117	700
13	1,3-dibromobenzene	0.05 mol-%, room temp., 2 h	100	1000	2000
14	1,4-dibromobenzene	0.05 mol-%, room temp., 5 h	100	400	2000
15	9,10-dibromoanthracene	0.1 mol-%, room temp., 4 h	100	250	1000
16	1,3,5-tribromobenzene	0.1 mol-%, room temp., 24 h	100	42	1000
17	4,4′-dibromobiphenyl	0.1 mol-%, room temp., 24 h	83	35	830

[a] Aryl halide (0.5 mmol), phenylboronic acid (0.75, 1.25 and 1.75 mmol for mono-, di- and tribromo derivatives, respectively), K_2CO_3 (1 mmol), MeOH (5 mL). [b] Percentage conversion to coupled product as determined by GC, based on aryl halides, and averaged over two runs. [c] Defined as mole product per mole of catalyst per hour. [d] Defined as mole product per mole of catalyst.

substituted derivative after 24 h (Table 4, entry 17). In contrast, the coupling reaction of 2-bromopyridine with phenylboronic acid was less successful and gave only moderate conversion (35%) after 6 h at room temperature (Table 4, entry 12). In most cases there was not much improvement in the conversions after a set period of time, which may be due to the deactivation of the catalyst (Table 4, entries 5, 6, 9, 11, 12 and 17).

The Suzuki cross-coupling reaction is strongly influenced by the solvent and base present in the reaction mixture. For example, replacing K_2CO_3 with Cs_2CO_3 or K_3PO_4 and employing non-polar solvents such as toluene and *n*-hexane gave low catalytic conversion rates. The homogeneous nature of the catalysis was checked by the classical mercury test.[19] Addition of a drop of mercury to the reaction mixture did not affect the conversion level of the reaction, which suggests that the catalysis is homogeneous in nature since heterogeneous catalysts would form an amalgam, and therefore be poisoned by the mercury.

Conclusions

The tertiary phosphane ligand **1** readily reacts with various Group 11 metal derivatives to give either tetranuclear clusters or a 2D polymeric sheet depending upon the reaction conditions and the stoichiometry of the reactants. With copper(I) halides, tetranuclear cubane complexes **2**–**4** were formed, whereas with AgCN a 2D polymeric sheet, involving week Ag–N (NMe nitrogen atom of $MeNC_4H_8N$-) interactions, was isolated. Similar reactions of **1** with AuCl(SMe_2) and silver(I) halides afforded mono- and dinuclear complexes **5** and **7**–**8**, respectively. Surprisingly, the ligand did not show multidentate behavior despite the presence of three terminal nitrogen atoms. The Pd^{II} complex **9** effectively catalyzes the Suzuki cross-coupling reactions of several aryl mono-, di-, and tri-bromides with phenylboronic acid at room temperature. Further reactions of ligand **1** with Group 10 metals and their catalytic utility in various other organic transformations are under active investigation in our laboratory.

Experimental Section

Reagents and Techniques: All experimental manipulations were performed under rigorous anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use. The gold(I) and silver(I) complexes **5**–**8**, were prepared under dark conditions by wrapping the reaction vessel with aluminum foil. The metal precursors CuX (X = Cl and Br),[20] AuCl(SMe_2),[21] and [M(COD)Cl_2] (M = Pd and Pt),[22] were prepared according to published procedures. AgX (X = Cl, Br and CN) were obtained from commercial sources and used without further purification. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded using Varian VXR 300 or VXR 400 spectrometers operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. The spectra were recorded in $CDCl_3$ solutions with $CDCl_3$ as an internal lock; in all cases positive shifts lie downfield of the standard. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument as KBr disks. The microanalyses were performed using a Carlo–Erba Model 1112 elemental analyzer. The melting points were observed in capillary tubes and are uncorrected. GC analyses were performed on a Perkin–Elmer Clarus 500 GC fitted with a packed column.

Synthesis of $P(NC_4H_8NMe)_3$ (1): A solution of *N*-methylpiperazine (20.7 g, 0.206 mol) in petroleum ether (20 mL; boiling range 60–80 °C) was added drop wise to a solution of phosphorus trichloride (4.72 g, 0.034 mol) also in petroleum ether (100 mL) at 0 °C with constant stirring. The reaction mixture was slowly warmed to room temperature, allowed to stir overnight, and then filtered through celite. The filtrate was concentrated under vacuum and stored at –30 °C for two days to give an analytically pure white crystals of **1**. Yield 80% (9.04 g); m.p. 78–80 °C. $C_{15}H_{33}N_6P$ (328.4): calcd. C 54.85, H 10.13, N 25.59; found C 54.82, H 10.10, N 25.51. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 9 H, NCH_3), 2.32 (br. s, 12 H, CH_2), 2.94 ppm (br. s, 12 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 112.2 ppm (s).

Synthesis of $[(CuCl)\{P(NC_4H_8NMe)_3\}]_4$ (2): A solution of cuprous chloride (0.059 g, 0.597 mmol) in acetonitrile (5 mL) was added drop wise to a solution of **1** (0.196 g, 0.597 mmol) also in acetonitrile (7 mL) with constant stirring. After stirring for 4 h, the solution was concentrated to 5 mL under vacuum and stored at room temperature overnight to give analytically pure pale green crystals of **2**. Yield 82% (0.209 g); m.p. 148–150 °C (dec.). $C_{60}H_{132}Cl_4Cu_4N_{24}P_4$ (1709.7): calcd. C 42.15, H 7.78, N 19.66; found C 42.19, H 7.75, N 19.64. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 36 H, NCH_3), 2.36 (br. s, 48 H, CH_2), 3.10 ppm (br. s, 48 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 98.9 ppm (s).

Synthesis of $[(CuBr)\{P(NC_4H_8NMe)_3\}]_4$ (3): Compound **3** was synthesized by a procedure similar to that for **2** using cuprous bromide (0.052 g, 0.360 mmol) and **1** (0.118 g, 0.360 mmol). Yield 88% (0.149 g); m.p. 210–214 °C (dec.). $C_{60}H_{132}Br_4Cu_4N_{24}P_4$ (1887.5): calcd. C 38.18, H 7.05, N 17.81; found C 38.11, H 7.08, N 17.78. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 36 H, NCH_3), 2.35 (br. s, 48 H, CH_2), 3.12 ppm (br. s, 48 H, CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 92.7 ppm (br. s).

Synthesis of $[(CuI)\{P(NC_4H_8NMe)_3\}_4]$ (4): Compound **4** was synthesized by a procedure similar to that for **2** using cuprous iodide (0.068 g, 0.357 mmol) and **1** (0.117 g, 0.357 mmol). Yield 95% (0.176 g); m.p. 150–152 °C (dec.). $C_{60}H_{132}Cu_4I_4N_{24}P_4$ (2075.5): calcd. C 34.72, H 6.41, N 16.20; found C 34.78, H 6.44, N 16.26. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 36 H, NCH_3), 2.33 (br. s, 48 H, CH_2), 3.17 ppm (br. s, 48 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 79.5 ppm (br. s).

Synthesis of $[(AuCl)\{P(NC_4H_8NMe)_3\}]$ (5): A CH_2Cl_2 (5 mL) solution of **1** (0.056 g, 0.169 mmol) was added drop wise to a solution of AuCl(SMe_2) (0.050 g, 0.169 mmol) also in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 4 h. The resulting solution was concentrated to 3 mL, layered with 3 mL of petroleum ether, and kept at –30 °C for one day to give **5** as an analytically pure white crystalline solid. Yield 79% (0.075 g); m.p. 156–158 °C (dec.). $C_{15}H_{33}AuClN_6P$ (560.8): calcd. C 32.12, H 5.93, N 14.98; found C 32.16, H 5.90, N 15.01. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 9 H, NCH_3), 2.30 (br. s, 12 H, CH_2), 3.15 ppm (br. s, 12 H, CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 102.3 ppm (s).

Synthesis of $[(AgCN)_2\{P(NC_4H_8NMe)_3\}]_n$ (6): A THF (3 mL) solution of **1** (0.061 g, 0.187 mmol) was added drop wise, at room temperature, to a suspension of AgCN (0.050 g, 0.373 mmol) also in THF (5 mL). The reaction mixture was stirred at room temperature

for 12 h and was then filtered through celite. The filtrate was concentrated and stored at room temperature for several days to give analytically pure white crystals of **6**. Yield 64% (0.071 g); m.p. 184–186 °C (dec.). $C_{17}H_{33}Ag_2N_8P$ (596.2): calcd. C 34.25, H 5.58, N 18.79; found C 34.26, H 5.60, N 18.81. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 9 H, NCH_3), 2.37 (br. s, 12 H, CH_2), 3.03 ppm (br. s, 12 H, CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 108.8 ppm (d, $^1J_{AgP}$ = 717 Hz). FT-IR (KBr disc:): $\tilde{\nu}$ = 2140 cm^{-1} (ν_{CN}).

Synthesis of [(AgCl){P(NC$_4$H$_8$NMe)$_3$}]$_2$ (7): A CH_2Cl_2 (3 mL) solution of **1** (0.115 g, 0.350 mmol) was added drop wise, at room temperature, to a suspension of AgCl (0.050 g, 0.350 mmol) also in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 24 h and was then filtered through celite. The filtrate was concentrated to 3 mL followed by the addition of petroleum ether (8 mL) to give a white precipitate of **7**. Recrystallization from a 1:1 dichloromethane/petroleum ether mixture at –30 °C afforded **7** as an analytically pure white crystalline substance. Yield 78% (0.129 g); m.p. 138–140 °C (dec.). $C_{30}H_{66}Ag_2Cl_2N_{12}P_2$ (943.5): calcd. C 38.19, H 7.05, N 17.81; found C 38.26, H 7.06, N 17.85. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 18 H, NCH_3), 2.38 (br. s, 24 H, CH_2), 3.09 ppm (br. s, 24 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 111.4 ppm (2d, $J^{109}{}_{AgP}$ = 929, $J^{107}{}_{AgP}$ = 804 Hz).

Synthesis of [(AgBr){P(NC$_4$H$_8$NMe)$_3$}]$_2$ (8): Compound **8** was synthesized by a procedure similar to that for **7** using silver bromide (0.061 g, 0.323 mmol) and **1** (0.106 g, 0.323 mmol). Yield 69% (0.115 g); m.p. 160–162 °C (dec.). $C_{30}H_{66}Ag_2Br_2N_{12}P_2$ (1032.4): calcd. C 34.90, H 6.44, N 16.28; found C 34.96, H 6.47, N 16.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 18 H, NCH_3), 2.35 (br. s, 24 H, CH_2), 3.09 ppm (br. s, 24 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 108.7 ppm (2d, $J^{109}{}_{AgP}$ = 854, $J^{107}{}_{AgP}$ = 743 Hz).

Synthesis of [{P(NC$_4$H$_8$NMe)$_3$}$_2$PdCl$_2$] (9): A CH_2Cl_2 (5 mL) solution of [Pd(COD)Cl_2] (0.036 g, 0.126 mmol) was added drop wise to a solution of **1** (0.083 g, 0.252 mmol) also in CH_2Cl_2 (7 mL). The reaction mixture was stirred at room temperature for 5 h to give clear yellow solution. The solution was concentrated to 3 mL, diluted with 3 mL of petroleum ether, and stored at –30 °C for 1 day to give an analytically pure yellow precipitate of **9**. Yield 95% (0.099 g); m.p. 106–108 °C (dec.). $C_{30}H_{66}Cl_2N_{12}P_2Pd$ (834.2): calcd. C 43.19, H 7.97, N 20.15; found C 43.12, H 7.89, N 20.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 18 H, NCH_3), 2.37 (br. s, 24 H, CH_2), 3.22 ppm (br. s, 24 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 89.5 ppm (s).

Synthesis of [{P(NC$_4$H$_8$NMe)$_3$}$_2$PtCl$_2$] (10): Compound **10** was synthesized by a procedure similar to that for **9** using [Pt(COD)Cl_2] (0.030 g, 0.080 mmol) and **1** (0.053 g, 0.160 mmol). Yield 87% (0.064 g); m.p. 140–142 °C (dec.). $C_{30}H_{66}Cl_2N_{12}P_2Pt$ (922.8): calcd. C 39.04, H 7.21, N 18.21; found C 39.10, H 7.25, N 18.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 18 H, NCH_3), 2.41 (br. s, 24 H, CH_2), 3.27 ppm (br. s, 24 H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 84.4 ppm (s, $^1J_{PtP}$ = 3236 Hz).

General Procedure for the Suzuki Cross-Coupling Reactions of Aryl Bromides with Phenylboronic Acid: In a two-necked round-bottomed flask, under an atmosphere of nitrogen, were placed the appropriate amounts of aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (0.138 g, 1 mmol) and methanol (5 mL). After stirring for 2 minutes, 0.05 mol-% of a freshly prepared stock solution of [{P(NC$_4$H$_8$NMe)$_3$}$_2$PdCl$_2$] (**9**) in dichloromethane was added. The mixture was stirred at room temperature, or refluxed under an atmosphere of nitrogen, and the course of the reaction was monitored by GC analysis. After completion of the reaction, the solvent was removed under reduced pressure. The residual mixture was diluted with H_2O (10 mL) and extracted with Et_2O or toluene (2 × 6 mL). The combined organic fractions were dried ($MgSO_4$), stripped of the solvent under vacuum, and the residue redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated with respect to the aryl halides.

Table 5. Crystallographic Information for Compounds **1**–**3** and **6**.

	1	**2**	**3**	**6**
Empirical formula	$C_{15}H_{33}N_6P$	$C_{60}H_{132}Cl_4Cu_4N_{24}P_4$	$C_{60}H_{132}Br_4Cu_4N_{24}P_4$	$C_{17}H_{33}Ag_2N_8P$
Fw	328.44	1709.74	1887.58	596.22
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a / Å	7.0087(8)	12.784(1)	12.828(1)	10.939(1)
b / Å	9.2380(1)	16.137(1)	16.213(1)	19.123(2)
c / Å	15.201(2)	22.238(2)	22.338(2)	11.686(1)
α / °	102.591(2)	76.991 (1)	76.632(1)	90
β / °	91.919(2)	78.755 (1)	78.554(1)	94.755(2)
γ / °	102.180(1)	68.661(1)	69.303(1)	90
V / Å^3	935.7(2)	4131.0(6)	4193.4(6)	2436.1(4)
Z	2	2	2	4
$\rho_{calcd.}$ / g cm^{-3}	1.166	1.375	1.495	1.626
μ (Mo-K_a) / mm^{-1}	0.154	1.274	3.033	1.692
F(000)	360	1808	1952	1200
Crystal size / mm	0.16 × 0.18 × 0.20	0.15 × 0.15 × 0.21	0.13 × 0.15 × 0.21	0.19 × 0.20 × 0.37
T / K	100	100	100	100
2θ range / °	1.4–28.3	1.4–28.3	1.4–28.3	2.0–27.8
Total number of reflections	7978	37158	37679	21123
Independent reflections	4232	19161	19457	5669
R_{int}	0.024	0.023	0.018	0.025
GoF (F^2)	1.02	1.04	1.05	1.05
R_1[a]	0.0466	0.0345	0.0279	0.0242
wR_2[b]	0.1247	0.0895	0.0718	0.0587

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [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 $P = (F_o^2 + 2F_c^2)/3$.

X-ray Crystallography: A crystal of each of the compounds **1**–**3** and **6** suitable for X-ray crystal analysis were mounted in a Cryoloop™ with a drop of Paratone oil, and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. Full spheres of data were collected, under the control of the SMART software package,[23] using 606 scans in ω (0.3° per scan) at f = 0, 120 and 240°, or a combination of three sets of 400 scans in ω (0.5° per scan) at f = 0, 90 and 180° plus two sets of 800 scans in f (0.45° per scan) at ω = –30 and 210°. The raw data were reduced to F^2 values using the SAINT+ software,[24] and global refinements of unit cell parameters using 4284–7898 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS).[25] All the structures were solved by direct methods and refined by full matrix least squares procedures using the SHELXTL program package.[26] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Pertinent crystallographic data and other experimental details are summarized in Table 5.

CCDC-658839 (for **1**), -658840 (for **2**), -658841 (for **3**) and -658842 (for **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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