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1D and 2D supramolecular structures of silver carborane dicyclohexylphosphine complexes constructed by C-H···H-B dihydrogen bonding interactions

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ABSTRACT

Five new carborane dicyclohexylphosphine complexes, $[Ag_2(\mu-I)_2\{1,2-(P Cy_2)_2-1,2-C_2B_{10}H_{10}\}_2]$ (1), $[Ag_2(SCN)_2\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}_2]_n \cdot CH_2CI_2$ (2), $[Ag(CIO_4)\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}_2] \cdot CH_2CI_2$ (3), $[Ag_2(\mu-NO_3)_2\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}_2] \cdot CH_2CI_2$ (4) and $[Ag(SC_6H_4COOH)\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}_2] \cdot CH_2CI_2$ (5), have been synthesized by the reactions of 1,2-bis(dicyclohexylphosphino)-1,2-dicarba-*closo*-dodecaborane with AgX (X = I, SCN, CIO_4, NO_3 and SC_6H_4COOH) in CH_2CI_2. The structures of the five complexes were characterized by elemental analysis, FT-IR, ¹H, ¹³C, ¹¹B and ³¹P NMR spectroscopy. X-ray structure analysis revealed that the structures of the complexes can be classified into three types. Complexes 1 and 4 are di- μ -X-bridged structures and complexes 3 and 5 are mononuclear structures, while complex 2 is a chain-like polymer. Complexes 1 and 2 form 2D supramolecular networks and complexes 3, 4 and 5 form 1D chains *via* C-H···H–B dihydrogen bonding interactions.

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1. Introduction

The C-substituted derivatives of dicarba-*closo*-dodecaborane $(1,2-C_2B_{10}H_{10})$, which was first reported in the early 1960s [1], have been intensely studied over the past several decades because of their interesting potential applications in many fields, such as boron neutron capture therapy (BNCT) [2–5], host–guest chemistry [6,7], materials science [8–10], catalysts [11] and coordination chemistry [12–15]. Recently, some diphosphine ligands of the type *closo*-1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ (R = phenyl, ethyl, isopropyl and ethoxy) have been synthesized [16]. Due to their excellent abilities to form stable five-member chelating rings between the ligand and metal atoms, these diphosphine ligands play an important role in the development of coordination chemistry [17–19].

In 1995, the first study of a new kind of interaction, the dihydrogen bond (DHB), was performed [20]. Since then, several types of DHBs have been reported, including $O-H\cdots H-B$, $N-H\cdots H-B$, $S-H\cdots H-B$, $C-H\cdots H-B$ [21,22]. With respect to $[C-H\cdots H-B]$ dihydrogen bonds, the ability of C–H bonds to form the dihydrogen bonds has been fairly well recognized. Our group also studied $C-H\cdots H-B$ dihydrogen bond systems involving isopropyl groups in previous work [23].

Related to the previous work, several groups have reported complexes of bis(diphenylphosphino)-o-carborane, including

palladium [18,19,24], copper [25], ruthenium [26], gold [27], silver [28], chromium, molybdenum and tungsten [29]. Our group was also interested in these types of ligands, and synthesized some complexes of 1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀ (R = Ph, i Pr) with transition metals such as nickel [30], palladium [31], silver [32], zinc [33] and copper [34]. In addition, the structure of the compound 1,2-(PCy₂)₂-1,2-C₂B₁₀H₁₀ has been reported [35]. To further study the effect of different substitute groups on the structure of the complexes formed, in this paper, we investigated the reactions of the ligand $1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}$ with AgX (X = I, SCN, ClO₄, NO₃ and SC₆H₄COOH), and obtained five silver complexes with the molecular formula $[Ag_2(\mu-I)_2\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}_2]$ (1), $[Ag_2(SCN)_2 \{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}_2]_n \cdot CH_2Cl_2$ (2), $[Ag(ClO_4)$ $\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}$ CH_2Cl_2 (3), $[Ag_2(\mu-NO_3)_2\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}$ CH_2Cl_2 (3), $[Ag_2(\mu-NO_3)_2\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}]$ $1,2-C_2B_{10}H_{10}$]·CH₂Cl₂ (4) and [Ag(SC₆H₄COOH){1,2-(PCy₂)₂-1,2- $C_2B_{10}H_{10}$ $]_2$ $] \cdot CH_2Cl_2$ (5). To the best of our knowledge, there has been no report on complexes of $1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}$, which are linked into 1D and 2D supramolecular structures through C-H···H-B dihydrogen bonds interactions between the cyclohexyl groups and the carborane cages.

2. Experimental

2.1. Materials

All the reactions were carried out under an atmosphere of dry dinitrogen. Dichloromethane, ethanol and *n*-hexane were dried with appropriate drying agents and distilled under dinitrogen prior



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to use. 1,2-(PCy_2)₂-1,2- $C_2B_{10}H_{10}$ was synthesized according to the literature [35]. All the other reagent chemicals were purchased and used as received.

2.2. Physical measurements

Infrared spectra were obtained from KBr pellets on a Nicolet-460 FT-IR spectrophotometer. Elemental analysis (C, H) was performed with a Perkin-Elemer 2400 II elemental analyzer. The ¹H, ¹³C, ¹¹B and ³¹P NMR spectra were recorded on a Varian Mercury 400 spectrometer in CDCl₃ solution with tetramethylsilane (TMS) as an internal standard at 400.15 and 100.63 MHz, respectively. The ¹³C spectra are broadband proton decoupled. The chemical shifts are reported in parts per million with respect to the references and are stated relative to external TMS for the ¹H and ¹³C NMR spectra. Chemical shift values for the ¹¹B NMR spectra were referenced to external BF₃·OEt₂ and ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄.

2.3. X-ray crystallography

Yellow crystals of complexes **1–5** were selected for diffraction analysis. The collections of intensity data were carried out on a Bruker Smart-1000 CCD diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structures were solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package [36]. The non- hydrogen atoms were refined anisotropically by fullmatrix least-squares calculations on F^2 . The *R*-factor of complex **3** was high, which might result from the weakly diffracting nature of the crystal. All H atoms were located from Fourier maps and were refined isotropically. The crystallographic data for the five complexes are summarized in Table 1.

2.4. Synthesis

2.4.1. Complex 1

Agl (23.5 mg, 0.10 mmol) and $1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}$ (53.5 mg, 0.10 mmol) were mixed in 10 ml CH₂Cl₂. The mixture was stirred for 6 h under a dry nitrogen atmosphere. After

 Table 1

 Details of the crystal parameters, data collection and refinement for complexes 1–5.

filtration, the solvent was volatilized in air and yellow crystals separated out about 1 week later (39.3 mg, 51%). M.p. 198–199 °C. FT-IR (cm⁻¹): 2921 (s), 2848 (m), 2570 (m), 1630 (w), 1445 (m), 1384 (m), 1072 (m), 719 (m). ¹H NMR (400.15 MHz, CDCl₃) δ (ppm): 1.35–2.23 (44H, Cy-H); ¹³C NMR (100.63 MHz, CDCl₃) δ (ppm): 26.0–39.0 (s, C, Cy-C); 77.312–76.680 (d, ¹*J*(C, P) = 252.8, 2C, carborane-C). ¹¹B NMR (CDCl₃) δ (ppm): –22.5 (6B), –27.9 (6B), –31.7 (8B). ³¹P{¹H} NMR (CDCl₃) δ (ppm): 45.66 (s, 4(PCy₂)). Anal. Calc. for C₅₂H₁₀₈Ag₂B₂₀l₂P₄: C, 40.44; H, 6.99. Found: C, 40.64; H, 7.10%.

By employing the same procedure described above, complexes **2–5** were prepared.

2.4.2. Complex **2**

(40.1 mg, 52%). M.p. 212–215 °C. FT-IR (cm⁻¹): 2929 (s), 2851 (m), 2567 (m), 2088 (m), 1629 (m), 1446 (s), 1384 (m), 1073 (m), 739 (m). ¹H NMR (400.15 MHz, CDCl₃) δ (ppm): 1.34–2.22 (44H, Cy-H); ¹³C NMR (100.63 MHz, CDCl₃) δ (ppm): 26.1–39.1 (s, 24C, Cy-C); 77.335–76.703 (d, ¹*J*(C, P) = 252.8, 2C, carborane-C). ¹¹B NMR (CDCl₃) δ (ppm): –22.6 (2B), –29.4 (2B), –32.5 (2B), –35.0 (4B). ³¹P{¹H} NMR (CDCl₃) δ (ppm): 45.60 (s, 2(PCy₂)). *Anal.* Calc. for C₅₆H₁₁₂Ag₂B₂₀Cl₄N₂P₄S₂: C, 42.66; H, 7.11; N, 1.78. Found: C, 42.44; H, 7.16; N, 1.70%.

2.4.3. Complex **3**

(40.6 mg, 49%). M.p. > 300 °C. FT-IR (cm⁻¹): 2932 (s), 2852 (m), 2576 (m), 1630 (w), 1446 (m), 1384 (w), 1073(m), 735 (m). ¹H NMR (400.15 MHz, CDCl₃) δ (ppm): 1.32–2.20 (44H, Cy-H); ¹³C NMR (100.63 MHz, CDCl₃) δ (ppm): 26.5–39.4 (s, 24C, Cy-C); 77.529–76.627 (d, ¹*J*(C, P) = 360.8, 2C, carborane-C). ¹¹B NMR (CDCl₃) δ (ppm): -23.5 (2B), -30.3 (2B), -35.3 (2B), -44.5 (4B). ³¹P{¹H} NMR (CDCl₃) δ (ppm): 27.07, 24.85 (s, 2(PCy₂)). *Anal.* Calc. for C₂₇H₅₆AgB₁₀Cl₃O₄P₂: C, 39.08; H, 6.76. Found: C, 39.20; H, 6.66%.

2.4.4. Complex **4**

(37.3 mg, 47%). M.p. 192–193 °C. FT-IR (cm⁻¹): 2928 (s), 2851 (m), 2574 (m), 1630 (w), 1449 (s), 1384 (m), 1073 (m), 732 (m). ¹H NMR (400.15 MHz, CDCl₃) δ (ppm): 1.33–2.21 (44H, Cy-H); ¹³C NMR (100.63 MHz, CDCl₃) δ (ppm): 26.6–39.5 (s, 24C, Cy-C); 77.312–76.680 (d, ¹/(C, P) = 252.8, 2C, carborane-C). ¹¹B NMR

	1	2	3	4	5
Empirical formula Formula weight	$C_{52}H_{108}Ag_2B_{20}I_2P_4$ 1543.00	$\begin{array}{l} C_{56}H_{112}Ag_{2}B_{20}Cl_{4}N_{2}P_{4}S_{2}\\ 1575.22 \end{array}$	C ₂₇ H ₅₆ AgB ₁₀ Cl ₃ O ₄ P ₂ 828.98	C ₅₄ H ₁₁₆ Ag ₂ B ₂₀ Cl ₄ N ₂ O ₆ P ₄ 1587.11	C ₃₄ H ₆₁ AgB ₁₀ Cl ₂ O ₂ P ₂ S 882.70
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	P2(1)/n	P2(1)/n	ΡĪ	ΡĪ	C2/c
Unit cell dimensions					
a (Å)	15.4620(18)	15.6140(15)	9.234(9)	12.0834(11)	38.012(3)
b (Å)	10.2101(12)	11.4001(12)	10.048(10)	13.7671(14)	11.3940(10)
c (Å)	23.532(3)	22.900(2)	23.09(2)	14.6367(16)	25.075(2)
α (°)	90	90	85.667(16)	114.055(2)	90
β(°)	102.983(2)	100.358(2)	89.487(15)	101.2800(10)	115.471(2)
γ (°)	90	90	63.690(14)	107.4010(10)	90
V (Å ³)	3620.0(7)	4009.8(7)	1915(3)	1975.8(3)	9804.7(15)
Ζ	2	2	2	1	8
$D ({ m Mg}{ m m}^{-3})$	1.416	1.305	1.438	1.334	1.196
F(0 0 0)	1560	1632	856	824	3664
Data/restraints/parameters	6365/0/361	7052/7/406	6469/1369/452	6864/0/415	86161/1/469
Goodness-of-fit on F ²	1.009	1.003	1.009	1.002	1.001
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0749$,	$R_1 = 0.0478,$	$R_1 = 0.1041$,	$R_1 = 0.0544,$	$R_1 = 0.0627, wR_2 = 0.1361$
	$wR_2 = 0.1654$	$wR_2 = 0.0981$	$wR_2 = 0.2598$	$wR_2 = 0.1501$	
R indices (all data)	$R_1 = 0.1317,$ $wR_2 = 0.1982$	$R_1 = 0.0493,$ $wR_2 = 0.1053$	$R_1 = 0.1519,$ $wR_2 = 0.2956$	R ₁ = 0.0916,wR ₂ = 0.1970	R ₁ = 0.1605,wR ₂ = 0.1570
Largest difference in peak and hole $(e \text{ Å}^{-3})$	1.609 and -1.154	0.873 and -0.650	1.330 and -1.159	0.792 and -0.732	0.773 and -0.388



Scheme 1. Preparation of complexes 1 and 4.



Scheme 2. Preparation of complex 2.



Scheme 3. Preparation of complexes 3 and 5.

(CDCl₃) δ (ppm): -19.1 (2B), -24.4 (8B), -28.1 (10B). ³¹P{¹H} NMR (CDCl₃) δ (ppm): 27.73, 27.57, 25.45, 25.30 (s, 4(PCy₂)). Anal. Calc.

for $C_{54}H_{116}Ag_2B_{20}Cl_4N_2O_6P_4$: C, 40.83; H, 7.31; N, 1.76. Found: C, 41.05; H, 7.39; N, 1.65%.

2.4.5. Complex 5

(39.7 mg, 45%). M.p. > 300 °C. FT-IR (cm⁻¹): 2921 (s), 2848 (m), 2570 (m), 1632 (m), 1445 (m), 1384 (m), 1072 (m), 739 (m). ¹H NMR (400.15 MHz, CDCl₃) δ (ppm): 1.29–2.17 (44H, Cy-H); ¹³C NMR (100.63 MHz, CDCl₃) δ (ppm): 26.8–39.8 (s, 24C, Cy-C); 77.320–76.680 (d, ¹*J*(C, P) = 256.0, 2C, carborane-C). ¹¹B NMR (CDCl₃) δ (ppm): -20.6 (2B), -25.6 (2B), -28.3 (2B), -32.3 (4B). ³¹P{¹H</sup> NMR (CDCl₃) δ (ppm): 27.72, 24.50 (s, 2(PCy₂)). *Anal.* Calc. for C₃₄H₆₁AgB₁₀Cl₂O₂P₂S: C, 46.22; H, 6.91. Found: C, 46.02; H, 6.82%.



Fig. 1. The crystal structure of complex 1. The H atoms have been omitted for clarity.



Fig. 2. The crystal structure of complex 4. The H atoms and solvent molecules have been omitted for clarity.

Table 2	
Selected bond lengths (Å) and angles (°) for complexes 1–3	5.

Complex 1			
P(1)-C(25)	1.88(1)	Ag(1)-p(2)	2.51(3)
P(2)-C(26)	1.88(1)	I(1)-Ag(1)	2.80(1)
C(25)-C(26)	1.88(2)	Ag(1) - P(1)	2.49(3)
P(1)-Ag(1)-P(2)	92.2(1)	I(1)-Ag(1)#1	2.87(1)
I(1)-Ag(1)-I(1)#1	101.5(4)		
Complex 2			
Ag(1) - N(1)	2.33(5)	P(1)-C(1)	1.88(5)
Ag(1) - P(2)	2.50(1)	P(2)-C(2)	1.88(5)
Ag(1) - P(1)	2.51(1)	C(1) - C(2)	1.88(7)
Ag(1)-S(1)	2.53(2)	P(2)-Ag(1)-P(1)	90.1(5)
Complex 3			
Ag(1) = O(1)	2.27(7)	P(2) - C(2)	1.86(1)
Ag(1) - P(1)	2.44(3)	P(1)-C(1)	1.86(1)
Ag(1)-P(2)	2.45(3)	C(1) - C(2)	1.85(1)
O(1) - Ag(1) - P(2)	135.7(2)	P(1)-Ag(1)-P(2)	94.3(1)
Complex 4			
$A_{\sigma}(1) = O(3)$	228(4)	P(2) = C(2)	184(6)
Ag(1) = P(1)	2.20(4) 2 41(2)	C(2) - C(1)	1.04(0)
Ag(1) - P(2)	2.11(2) 2.46(2)	P(1) - C(1)	1.86(5)
O(3) - Ag(1) # 1	2.47(4)	P(1) = Ag(1) = P(2)	961(5)
O(3) - Ag(1) - O(3) # 1	72.5(1)	1(1) 1.8(1) 1(2)	0011(0)
Complex 5	220(2)	D(2) = C(1)	1.05(0)
Ag(1) - S(1)	2.39(3)	P(2) = C(1)	1.85(9)
Ag(1) - P(1) Ag(1) - P(2)	2.40(3)	C(1) - C(2) S(1) C(27)	1.87(1) 1.77(1)
P(1) C(2)	2.47(2) 1.92(0)	S(1) - C(27) S(1) - Ag(1) - D(1)	121 9(0)
F(1) = C(2) $S(1) = A_{\alpha}(1) = D(2)$	126 1(0)	D(1) - Ag(1) - P(1)	02.0(9)
S(1) - Ag(1) - F(2)	130.1(9)	$\Gamma(1) - Ag(1) - \Gamma(2)$	52.0(0)

The symmetry transformations used to generate equivalent atoms for complex 1: # 1 - x + 1, -y + 2, -z; complex 2, # 1 - x + 1, -y + 1, -z; complex 4, # 1 - x + 1/2, y + 1/2, -z + 1/2.

3. Results and discussion

3.1. Synthesis of complexes

All the complexes are obtained by the reactions of $1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}$ with AgX (X = I, SCN, ClO₄, NO₃ and SC₆H₄COOH) in CH₂Cl₂ solution under the protection of dry N₂ at room temperature. The as-obtained five complexes can be classified into three types according to their structural characteristics. Complexes **1** and **4** possess di- μ -X-bridged dimer structures (X = I, NO₃) (Scheme 1). Complex **2** is a chain-like polymer composed of repeating structural units [Ag₂(SCN)₂{1,2-(PCy₂)₂-1,2-C₂B₁₀H₁₀}] (Scheme 2). Complexes **3** and **5** are mononuclear structures (Scheme 3). These phenomena can be attributed to the difference of the coordination anions, which has also been reported by Francesco Caruso [28].

3.2. IR spectra

The IR spectra of these five complexes are very similar. Absorptions characteristic of terminal B–H vibrations are exhibited at 2567, 2576, 2574 and 2570 cm⁻¹ for complexes **1–5**, respectively, which lie in the normal range for B–H vibrations of 2645–2450 cm⁻¹ [37]. Also, all the B–H vibration absorptions for complexes **1–5** are almost equal to that of the free ligand (2586 cm⁻¹), indicating that the coordination of the metal to the free ligand has no influence on the B–H group. The peak at 1072 cm⁻¹ can be attributed to the absorption of $v_{C(Cyc)-P}$. The absorption at approximate 736 cm⁻¹ shows the existence of the deformation of the cage [24]. The absorptions centered at



Fig. 3. The zigzag chain in complex 1. The H atoms have been omitted for clarity.

1384 cm⁻¹ may be attributed to the v_{C-H} scissoring vibration of the CH₂ group. A middle absorption at about 2088 cm⁻¹ for complex **2** should be attributed to the C \equiv N bond of SCN⁻.

3.3. NMR spectra

All the complexes were characterized by ¹H and ¹³C NMR spectroscopy. The ¹H NMR (400.15 MHz) showed a resonance at ca. 1.25–2.69 ppm, which could be assigned to the H atoms of the $P(Cy_2)_2$ group. In the ¹³C NMR spectra (100.63 MHz), the resonance at ca. $\delta = 26.0-40.0$ ppm can be assigned to the carbon atom of the cyclohexyl, and $\delta = 78.0-76.0$ ppm are the carborane cage C atoms [38]. The ¹¹B NMR spectra display a 3:3:4 splitting pattern for complex **1**, 1:1:1:2 for complexes **2**, **3** and **5**, and 1:4:5 for complex **4**. The ³¹P NMR spectra of complexes **1** and **2** showed a resonance at 45.66 and 45.60 ppm, respectively. The ³¹P NMR spectra display a 1:1 splitting pattern for complexes **3** and **5**, and 1:1:1:1 for complex **4**.

3.4. Description of the crystal structures

3.4.1. The crystal structures of complexes 1 and 4

The crystal structures of complexes 1 and 4 are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles are listed in Table 2. Complexes 1 and 4 possess binuclear structures with a rhomboid core consisting of two Ag atoms and two bidentate ligands. Each Ag atom has the same environment because complexes **1** and **4** are centrosymmetric. The Ag atom is tetrahedrally surrounded by two P atoms of the ligand and the other two donors are di- μ -X bridged atoms (X = I or NO₃). The conformation of the two complexes are similar with the complex $[Ag_2(\mu-Cl)_2\{1,2 (PPh_2)_2-1, 2-C_2B_{10}H_{10}_2$ [39]. In complex 1, the Ag(1)-I(1) and Ag(1)-P(1) bond lengths are 2.87(1) and 2.49 (3) Å, which agree well with the corresponding bond lengths of 2.89(1) and 2.49(2) Å in the complex $[Ag_2I_2(o-PP)]$ (o-PP = 1,2-Bis[(diphenyl phosphino)methyl]benzene) [28]. The P-Ag-P angle is 92.2(1)° in complex **1**, which is slightly larger than the corresponding angle $(89.8(5)^{\circ})$ in the complex $[Ag_2(\mu-Cl)_2\{1,2-(PPh_2)_2-1,2-C_2B_{10}H_{10}\}_2]$.



Fig. 4. Two-dimensional hexagonal grid of complex 1 formed by intermolecular C-H···H-B dihydrogen bonding interactions.



Fig. 5. The zigzag chain in complex 4 formed by intermolecular C-H···H-B dihydrogen bonding interactions.

In complex **4**, the P–Ag–P angle is 96.1(5)°, which is larger than the corresponding value of complex **1**. This may result from the difference of the size of the atoms (I \gg O). A similar change of P–Ag–P angles has also been observed in the previous literature [28]. The distance of the Ag(1)–O(3) bond is 2.28(4) Å, which is shorter than the corresponding bond reported for the complex [Ag₂(NO₃)₂ (*m*-PP)] (2.47(2) Å, *m*-PP = 1,3-bis[(diphenylphosphino)methyl] benzene) [30]. The orientation of the nitrates relative to the

 Ag_2O_2 core is the same in complex **4**, which is different from that in the complex $[Ag_2(NO_3)_2(m-PP)]$.

Based on the dihydrogen bonds C(20)–H(20A)···H(6)–B(6), the structure of complex **1** can be better described as a two-dimensional hexagonal grid wherein the bridged molecules [Ag₂ (μ -I)₂{1,2-(PCy₂)₂-1,2-C₂B₁₀H₁₀}] are linked into a 1D chain (Fig. 3). Adjacent chains are further cross-linked by the same contacts giving rise to a 2D hexagonal grid-like sheet with intragrid



Fig. 6. The crystal structure of complex 2. The H atoms and solvent molecules have been omitted for clarity.



Fig. 7. Two-dimensional hexagonal grid of the complex 2 formed by intermolecular C-H...H-B dihydrogen bonding interactions.

 $M \cdots M$ separations of 10.21 and 16.28 Å (Fig. 4). In complex **4**, adjacent molecules are linked into a 1D chain *via* C(18)–H(18B)···H(6)–B(6), as is shown in Fig. 5. The distance between adjacent molecules is 14.73 Å. There are two dihydrogen bonds between adjacent molecules, which are parallel to each other.

3.4.2. The crystal structure of complex 2

The crystal structure of complex **2** is illustrated in Fig. 6, and selected bond lengths and angles are listed in Table 2. The unit $[Ag\{1,2-(PCy_2)_2-1,2-C_2B_{10}H_{10}\}]$ is linked to a 1D coordination polymer chain by the SCN⁻ ligands. The Ag atom is tetracoordinated by



Fig. 8. The crystal structure of complex 3. The H atoms and solvent molecules have been omitted for clarity.



Fig. 9. The crystal structure of complex 5. The H atoms and solvent molecules have been omitted for clarity.

one S atom, one N atom of SCN and the donor phosphorus atoms of one ligand. The Ag atoms in the chain are alternately arranged along zigzag chains, as shown in Fig. 6. Adjacent polymer chains are assembled into a 2D hexagonal grid *via* C(16)–H(16B)···H(6)– B(6) interactions, as shown in Fig. 7. Every hexagonal grid includes six Ag ions and each vertex contains one crystallographic Ag ion, with Ag···Ag distances of 6.55, 11.40 and 12.56 Å. Being similar to the above complexes, the dihydrogen bonds between adjacent chains are parallel to each other.

3.4.3. The crystal structures of complexes 3 and 5

The crystal structures of complexes **3** and **5** are illustrated in Figs. 8 and 9. Selected bond lengths and angles are listed in Table 2. A perspective view of the structural units of complexes **3** and **5** is displayed in Figs. 8 and 9, respectively. The Ag atom is three coordinated, in which two positions are occupied by the chelating *closo* diphosphine ligand 1,2-(PCy₂)₂-1,2-C₂B₁₀H₁₀, and the other one comes from the O atom of ClO_4^- or the S atom of $SC_6H_4COOH^-$. In complexes **3** and **5**, adjacent molecules are linked together into one-dimensional zigzag chains *via* dihydrogen bonds, as shown in Figs. 10 and 11.

On the whole, the Cc–Cc bond lengths (the carbon of the carborane skeleton) in the five complexes are 1.88(2), 1.88(7), 1.85(1), 1.91(8) and 1.87(3) Å, respectively, which are slightly larger than the corresponding distance of 1.6911(10) Å in 1,2-(PCy cl₂)₂-1,2- $C_2B_{10}H_{10}$, suggesting that the coordination with the metal atom has obvious influences on this distance. The P(1)–C(1)–C(2)–P(2) torsion angles are only $-1.5(12)^\circ$, $0.9(5)^\circ$, $0.5(10)^\circ$, $2.4(5)^\circ$ and $0.4(9)^\circ$ in the complexes **1–5**, respectively, while the angle in the free ligand is 10.9(4)°, indicating that the symmetry of the ligands in the five complexes has obviously changed and approached $C_{2\nu}$ symmetry [40]. Besides, the P(1)–C(1)–C(2)–P(2) torsion angles in the corresponding values in complexes **2** (0.9(5)°), **3** (0.5(10)°) and **5** (0.4(9)°). The bridged structures of complexes **1** and **4** also have a great influence on the torsion angles.

3.5. Dihydrogen bond

Table 2

Selected distances and angles for complexes 1-5 relating to the intermolecular DHB are shown in Table 3. The distances of the two H...H interactions for complexes 1–5 range from 2.26 to 2.39 Å, which are slightly shorter than the sum of the van der Waals radii of H and H (2.4 Å) [17]. The distances of $C(20) \cdots B(6)$ and $C(16) \cdots B(6)$ are 3.89 and 3.92 Å for complexes **1** and **2**, which are similar to the distances of $C \cdots B$ (3.93, 3.94 and 3.91 Å) for $[Cu_2(\mu-X)_2(1,2-(P^iPr_2)_2-1,2-C_2B_{10}H_{10})_2]$ (X = Cl, Br, I) [24]. The $C(18) \cdots B(8)$ distance in complex **5** is 4.08 Å, which is similar the $C \cdot \cdot \cdot B$ distances of 4.10 Å in to $[(C_2B_{10}H_{11})]$ $C_6H_4(C_2B_{10}H_{10})C_6H_4(C_2B_{10}H_{11})$ [41]. In complex 4, the $C(18) \cdots B(6)$ distance is 3.72 Å, which is slightly larger than the $C(6) \cdots B(18')$ distance, with the value of 3.59 Å, in the complex 8,9'-[closo-{3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₀}] [42]. The C-H-H angle (163.5°) and the B-H···H angle (134.3°) of C(18)-H(18A)···H(8)-

able J									
Selected	distances	(Å) an	1 angles	(°) of	complexes	1-5	related	to	intermolecular
DHBs.									

Complex	C−H···H−B	$H{\cdots}H$	$C{\cdots}B$	$C\text{-}H\text{-}\cdot\text{H}$	$H{-}H{\cdot}{\cdot}{\cdot}B$
1	$C(20)-H(20A)\cdots H(6)-B(6)$	2.32	3.89	147.8	114.4
2	$C(16)-H(16B)\cdots H(6)-B(6)$	2.36	3.92	139.7	133.3
3	$C(8)-H(8B) \cdot \cdot \cdot H(10)-B(10)$	2.39	3.69	110.5	116.8
4	$C(18)-H(18 B)\cdots H(6)-B(6)$	2.26	3.72	130.4	132.5
5	C(18)-H(18A) + H(8)-B(8)	2.29	4.08	163.5	134.3
	$C(5)-H(5) \cdot \cdot \cdot H(3A)-B(3)$	2.23	4.28	163.8	174.6



Fig. 10. The zigzag chain in complex **3** formed by intermolecular C-H···H-B dihydrogen bonding interactions.



Fig. 11. The zigzag chain in complex 5 formed by intermolecular C-H···H-B dihydrogen bonding interactions.

B(8) in complex **5** are consistent with other typical DHBs described as X-H···H-M (X is a typical electronegative atom and M is a transition metal or boron atom) [20].

4. Conclusion

In this work, the reactions between the closo-carborane dicyclohexylphosphine ligand 1,2-(PCy₂)₂-1,2-C₂B₁₀H₁₀ and Ag(I) salts, under the protection of dry N_2 at room temperature, have been investigated for the first time. Five silver carborane complexes were obtained. The structure analyses of complexes 1-5 reveal that the different coordination anions lead to different structures of complexes 1–5. It was also found that C–H···H–B contacts exist in these five complexes. Because of the different orientations of the DHBs, the complexes are linked into 1D and 2D supramolecular structures via dihydrogen bonds.

supplementary data

CCDC 768113, 749847, 768109, 768114 and 768115 contain the supplementary crystallographic data for $[Ag_2(\mu-I)_2\{1,2-(PCy_2)_2 1,2-C_2B_{10}H_{10}$], [Ag₂(SCN)₂{1,2-(PCy₂)₂-1,2-C₂B₁₀H₁₀}]_n·CH₂Cl₂, $[\text{Ag}(\text{ClO}_4)\{1,2\text{-}(\text{PCy}_2)_2\text{-}1,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2\{1,2\text{-}1,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_{10}]\cdot\text{CH}_2\text{Cl}_2, \qquad [\text{Ag}_2(\mu\text{-}\text{NO}_3)_2(1,2\text{-}1)_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_2,2\text{-}\text{C}_2\text{B}_{10}\text{H}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2\text{C}_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)_2,2\text{-}\text{C}_2\text{C}_2,2\text{-}1)$ (PCy₂)₂-1,2-C₂B₁₀H₁₀}₂]·CH₂Cl₂ and [Ag(SC₆H₄C OOH){1,2-(PCy₂)₂- $1,2-C_2B_{10}H_{10}$]·CH₂Cl₂. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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