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Synthesis and spectroscopy of *cis*-configured mononuclear palladium(II) and platinum(II) complexes of chalcogeno *o*-carboranes and structures of $[Pt(SCb^oPh)_2(dppm)]$, $[Pt(SeCb^oPh)_2(dppm)]$, $[Pt(SCb^oS)(PMe_2Ph)_2]$ and $[Pt(SCb^oS)(PMePh_2)_2]$

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ABSTRACT

The reactions of $[MCl_2(P^{\cap}P)]$ and $[MCl_2(PR_3)_2]$ with 1-mercapto-2-phenyl-*o*-carborane/NaSeCb^{o}Ph and 1,2-dimercapto-*o*-carborane yield mononuclear complexes of composition, $[M(SCb^oPh)_2(P^{\cap}P)]$, $[M(SeCb^oPh)_2(P^{\cap}P)]$ (M = Pd or Pt; $P^{\cap}P$ = dppm (bis(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane) or dppp (1,3-bis(diphenylphosphino)propane)) and $[M(SCb^oS)(PR_3)_2]$ ($2PR_3$ = dppm, dppe, $2PEt_3$, $2PMe_2Ph$, $2PMePh_2$ or $2PPh_3$). These complexes have been characterized by elemental analysis and NMR (^1H, ^{31}P, ^{77}Se and ^{195}Pt) spectroscopy. The $^1J(Pt-P)$ values and ^{195}Pt NMR chemical shifts are influenced by the nature of phosphine as well as thiolate ligand. Molecular structures of $[Pt(SCb^oPh)_2(dppm)]$, $[Pt(SeCb^oPh)_2(dppm)]$, $[Pt(SCb^oS)(PMe_2Ph)_2]$ and $[Pt(SCb^oS)(PMePh_2)_2]$ have been established by single crystal X-ray structural analyses. The platinum atom in all these complexes acquires a distorted square planar configuration defined by two *cis*-bound phosphine ligands and two chalcogenolate groups. The carborane rings are mutually *anti* in $[Pt(SCb^oPh)_2(dppm)]$ and $[Pt(SeCb^oPh)_2(dppm)]$.

1. Introduction

The synthesis and characterization of platinum group metal chalcogenolate complexes continue to be an active area of research. There are several obvious reasons for this sustained interest as these complexes display novel structures [1–4] and have relevance in catalysis [5–10]. More recently they have shown potential as single source precursors for the synthesis of metal chalcogenides [11–13] and anti-cancer agents, e.g. both *cis*- and *trans*-PtP_2S_2 core (P_2 = mono or chelating phosphines) exhibit promising anti-proliverative properties [14,15]. The high propensity of organo-chalcogenolate ligand, in general, leads to M-ER-M bridges as a consequence the resulting complexes are isolated as oligomeric, insoluble or sparingly soluble, non-volatile species. Several strategies have been adopted to stabilize monomeric frameworks. These include (i) use of chelating phosphine ligands [16], (ii) chelating thiolate ligands $(S\text{-}R\text{-}S)^{2-}$ [17,18], (iii) bulky chalcogenolate ligands [19,20] and internally functionalized chalcogenolate ligands [5,21–23]. Monomeric complexes, $[M(SR)_2(PR_3)_2]$ have been studied with reference to cis- and trans-isomerization process [24] and in fact the cis isomer is readily isomerized to trans form in solution [24–28]. The DFT calculations on model complexes, $[Pt(SeR)_2(PH_3)_2]$ revealed that the cis isomers lie at higher energy than that of the trans isomer [25]. Mononuclear chalcogenolate complexes with cis configuration have been used as molecular tactons for the preparation of bi- and high-nuclearity complexes [29–34]. The cis-$[M(ER)_2(PR_3)_2]$ have been shown to be catalytically active and catalytic activity degrades with time due to isomerization into trans form [8].

The chemistry of functionalized icosahedral-*closo*-carboranes has attracted considerable attention due to their use in organic synthesis [35,36] and potential applications in medicine [37–42] and materials science [43,44]. The unique rigidity and gross steric bulk, which is comparable to rotating benzene, of carborane offer several possibilities and can aid in the formation and stabilization of novel structures. For instance, steric congestion of 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolate ($E_2C_2B_{10}H_{10}$; E = S or Se)

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ligands assists in stabilizing coordinatively unsaturated 16-electron half-sandwich mononuclear complexes, $[Cp^{\#}M(E_2C_2B_{10}H_{10})]$ ($Cp^{\#}$ = Cp or Cp^{*}; M = Co, Rh, Ir) and [(*p*-cymene) $M(E_2C_2B_{10}H_{10})$] (M = Ru or Os) complexes which exhibit rich reaction chemistry [45–52].

With the above perspective and in pursuance of our interest in platinum metal chalcogenolate chemistry we have isolated several mononuclear Pd and Pt complexes derived from carborane chalcogenolate ligands and characterized them by NMR spectroscopy and some by X-ray crystallography.

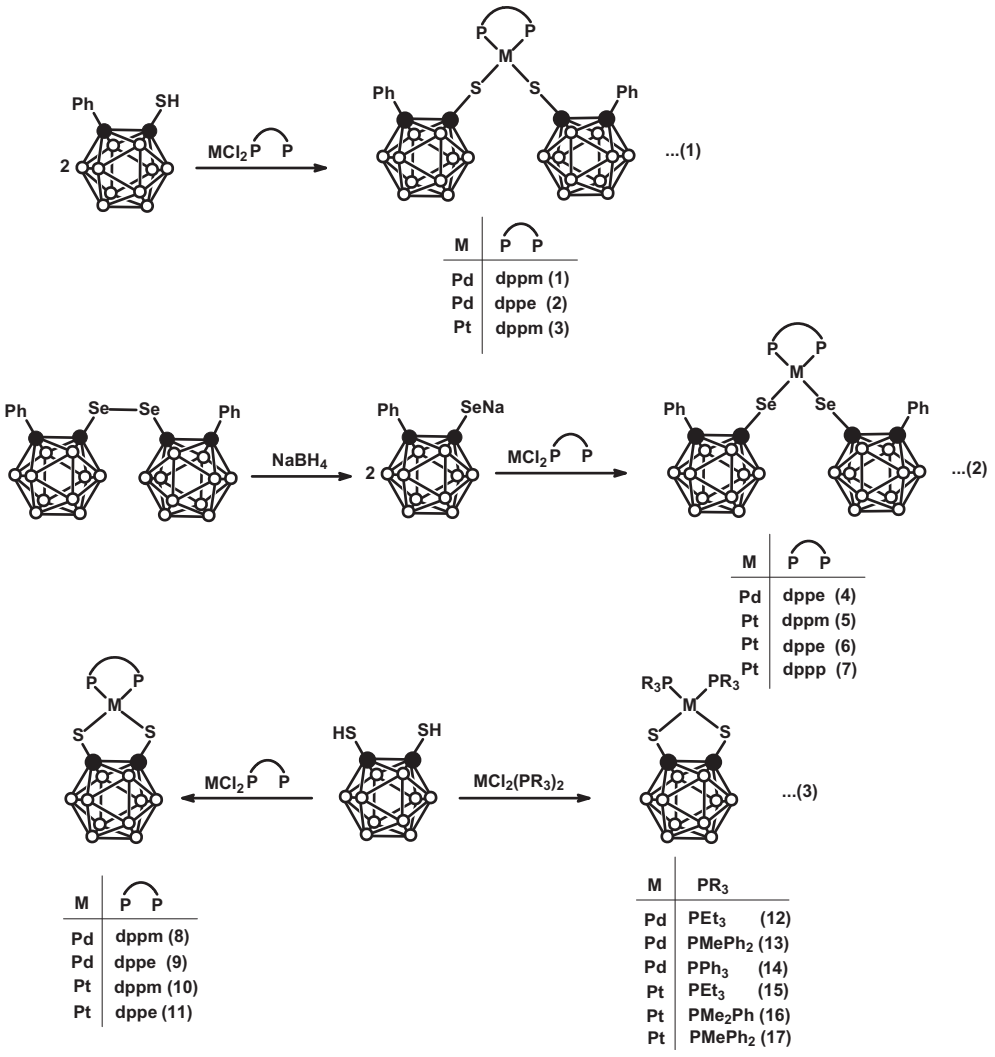
2. Results and discussions

2.1. Synthesis and spectroscopy

The reactions of $[MCl_2(P^{\cap}P)]$ with 1-mercapto-2-phenyl-*o*-carborane in the presence of pyridine as HCl scavenger yield mononuclear thiolate complexes of composition, $[M(SCb^{o}Ph)_2(P^{\cap}P)]$ (Scheme 1). Analogous selenolate complexes, $[M(SeCb^{o}Ph)_2(P^{\cap}P)]$ (M = Pd or Pt; $P^{\cap}P$ = dppm, dppe or dppp), have been isolated by treatment of $[MCl_2(P^{\cap}P)]$ with $NaSeCb^{o}Ph$, prepared by reductive cleavage of Se–Se bond of $(PhCb^{o}Se)_2$ by methanolic $NaBH_4$. The reactions of $[MCl_2(P^{\cap}P)]$ and $[MCl_2(PR_3)_2]$ with one equivalent of 1,2-dimercapto-*o*-carborane in the presence of pyridine afforded mononuclear complexes containing chelating dithiolate ligand. These complexes were isolated as yellow (in case of palladium) or white (in case of platinum) crystalline solids and could be crystallized from appropriate solvent mixtures in 51–85% yield.

The ^{1}H NMR spectra of these complexes showed expected resonances and peak multiplicities. The $^{77}Se\{^{1}H\}$ NMR spectra showed a doublet due to coupling with a ^{31}P nucleus of the phosphine trans to the selenolate ligand. The magnitude of $^{2}J(^{77}Se–^{31}P)$ is typical of palladium and platinum complexes bearing phosphine ligands [18,53,54]. The ^{31}P NMR spectra of palladium complexes displayed single resonances while the resonances for platinum complexes were flanked by ^{195}Pt satellites. The magnitude of $^{1}J(^{195}Pt–^{31}P)$ is reduced significantly from the corresponding dichlorides owing to strong trans influence of the chalcogen ligand. The $^{195}Pt\{^{1}H\}$ NMR spectra exhibited a triplet in the region δ −3892 to −4949 ppm due to coupling with two equivalent ^{31}P nuclei. The following salient trends are evident from the ^{31}P and ^{195}Pt NMR spectra of platinum complexes (Table 1):

- The magnitude of $^{1}J(Pt–P)$ in selenolate complexes is slightly larger than the corresponding thiolate derivatives. Similarly the ^{195}Pt NMR resonances of selenolate complexes are more shielded than the corresponding thiolate derivative [e.g., $[Pt(ECb^{o}Ph)_2(dppm)]$; ^{195}Pt NMR δ = −4063 (E = S) and −4289 (E = Se)]. This may be attributed to greater nucleophilicity of selenolate ligand.



Scheme 1.

Table 1
$^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectral data for platinum chalcogenolate complexes in $CDCl_3$.

Complex	^{31}P NMR Data		^{195}Pt NMR
	δ in ppm	^1J(Pt–P) in Hz	δ in ppm
[Pt(SCb°Ph)$_2$(dppm)] (**3**)	−52.6	2605	−4063
[Pt(SeCb°Ph)$_2$(dppm)] (**5**)	−55.7	2649	−4289
[Pt(SeCb°Ph)$_2$(dppe)] (**6**)	41.4	2994	−4949
[Pt(SeCb°Ph)$_2$(dppp)] (**7**)	−11.5	2840	–
[Pt(SCb°S)(dppm)] (**10**)	−46.4	2382	−3892
[Pt(SCb°S)(dppe)] (**11**)	44.6	2796	−4460
[Pt(SCb°S)(PEt$_3$)$_2$] (**15**)	7.6	2775	−4437
[Pt(SCb°S)(PMe$_2$Ph)$_2$] (**16**)	−17.6	2784	−4358
[Pt(SCb°S)(PMePh$_2$)$_2$] (**17**)	-1.5	2848	−4381
[Pt(SCb°Ph)$_2$(PMe$_2$Ph)$_2$] (**18**)	−16.3	3031	−4572
[Pt(SeCb°Ph)$_2$(PMe$_2$Ph)$_2$][a]	−19.5	3022	–
[Pt(SeCb°Ph)$_2$(PMePh$_2$)$_2$][a]	-7.8	3054	–

[a] From reference [55].

- The ^1J(Pt–P) values and ^{195}Pt NMR chemical shifts are influenced by the nature of phosphine as well as thiolate ligand. The magnitude of ^1J(Pt–P) and shielding of the ^{195}Pt NMR resonance increased in the following order: chelating phosphine and chelating dithio ligand > chelating phosphine and monodentate thio ligand > monodentate phosphine and chelating dithio ligand > monodentate phosphine and monodentate thio ligand.

2.2. Molecular structures

Molecular structures of [Pt(SCb°Ph)$_2$(dppm)] (**3**), [Pt(SeCb°Ph)$_2$(dppm)] (**5**), [Pt(SCb°S)(PMe$_2$Ph)$_2$] (**16**) and [Pt(SCb°S)(PMePh$_2$)$_2$] (**17**) have been established by single crystal X-ray diffraction analyses. ORTEP drawings with crystallographic numbering scheme are given in Figs. 1–4 while selected bond lengths and angles are summarized in Tables 2–5. The platinum atoms in all these complexes acquire a distorted square planar configuration defined by *cis*-"E$_2$P$_2$" (E = S or Se) donor atoms. The

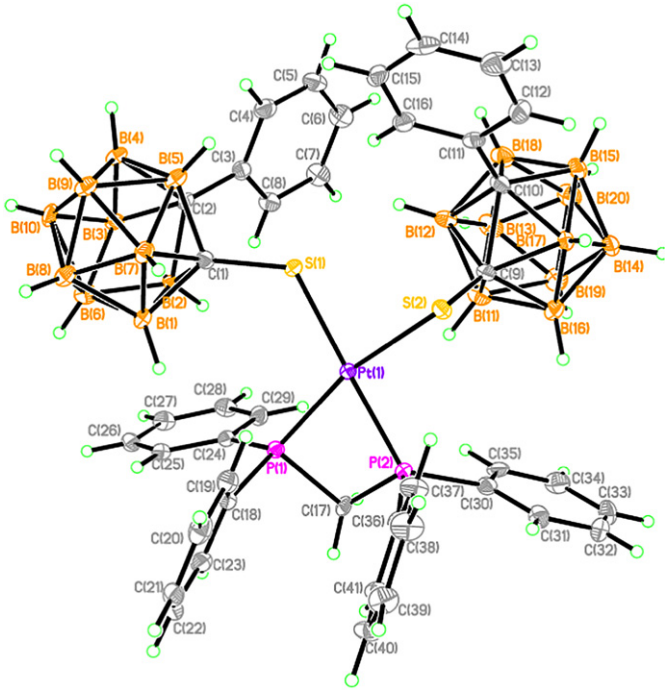


Fig. 1. Structure of [Pt(SCb°Ph)$_2$(dppm)] (**3**).

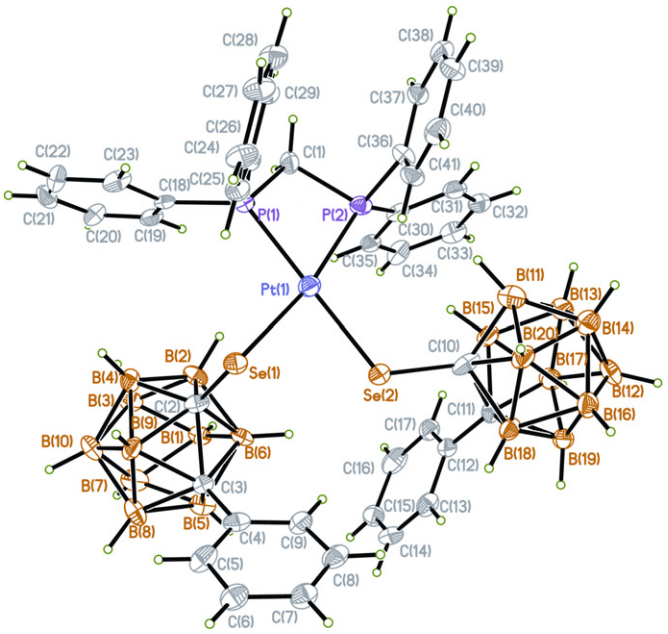


Fig. 2. Structure of [Pt(SeCb°Ph)$_2$(dppm)] (**5**).

Pt–P distances (~2.27 Å) in all these complexes are similar and are in accord with the literature values [29,55]. The Pt–S (2.32–2.38 Å) and Pt–Se distances are well within the range reported for platinum chalcogenolate complexes [29,55]. These distances are, however, slightly longer than those complexes containing chalcogenolate ligand trans to halide as in [PtCl(SCH$_2$CHMeNMe$_2$)(PMe$_2$Ph)] (Pt–S = 2.235 (2) Å) [33] and [Pt$_3$Cl$_4$(SeCH$_2$CH$_2$NMe$_2$)$_2$(PEt$_3$)$_2$] (Pt–Se = 2.3775 (8) Å) [56] owing to the strong trans influence of the phosphine ligand which is trans to chalcogenolate ligand in the present complexes. The Pt–Se distances can, however, be compared with those complexes containing selenolate ligand trans to strong trans influencing ligand as in [Pt$_3$(SeCH$_2$CH$_2$NH$_2$)$_2$Cl$_3$(PPr$_3$)$_3$]Cl (Pt$_2$–Se = 2.4211 (15) and 2.4630 (16) Å) [57]. The C–S (av. 1.77 Å) and C–Se (av. 1.93 Å) in these complexes can be compared with the corresponding distances reported in mercapto- and seleno-carborane complexes [55,58].

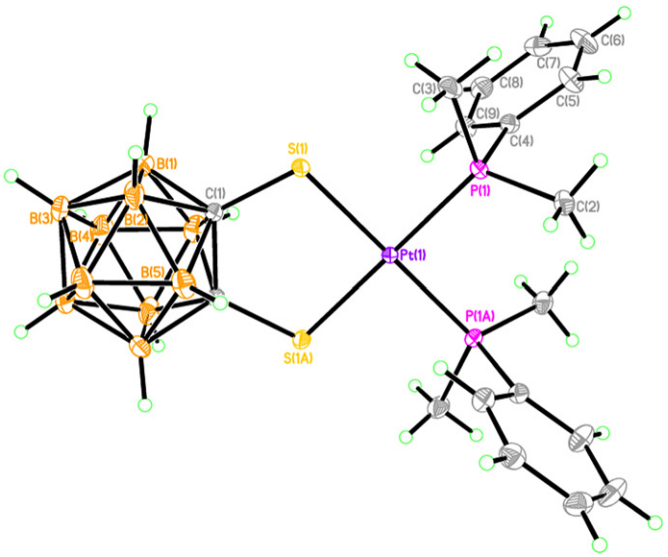


Fig. 3. Structure of [Pt (SCb°S)(PMe$_2$Ph)$_2$] (**16**).

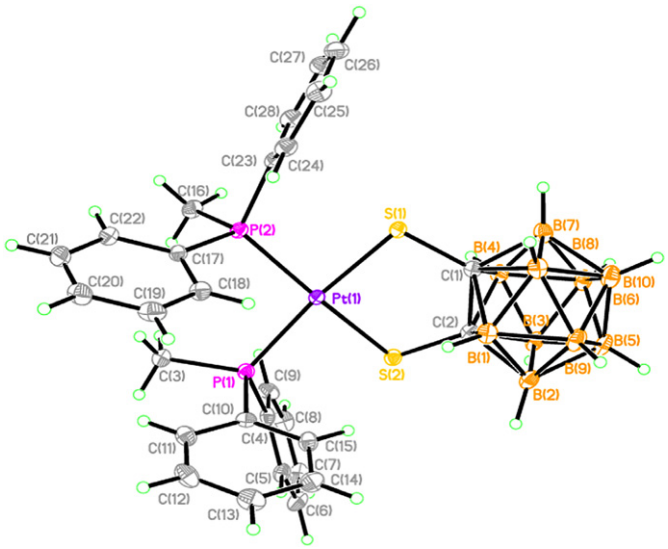


Fig. 4. Structure of [Pt(SCb^{o}S)(PMePh$_2$)$_2$] (**17**).

The complexes, [Pt(SCb^{o}Ph)$_2$(dppm)] (**3**) and [Pt(SeCb^{o}Ph)$_2$(dppm)] (**5**) have isomorphous structures. The P–Pt–P and E–Pt–E (E = S or Se) angles in two complexes are similar. To avoid steric crowding, the carborane rings are mutually anti, one lying above and another below the platinum square plane. A similar configuration has been reported for [Pt(SeCb^{o}Ph)$_2$(PMe$_2$Ph)$_2$] [55]. One of the Pt–E bonds is significantly longer (0.056 (for E = S) and 0.074 (for E = Se) Å) than the other. The two Pt–Se distances in complexes containing monodentate phosphine, like [Pt(SeCb^{o}Ph)$_2$(PMe$_2$Ph)$_2$] [55], differ only slightly (0.015 Å).

The dithio-*o*-carborane in [Pt(SCb^{o}S)(PMe$_2$Ph)$_2$] (**16**) and [Pt(SCb^{o}S)(PMePh$_2$)$_2$] (**17**) forms a five membered chelate ring. Various angles in two molecules are similar. The complex [Pt(SCb^{o}S)(PMe$_2$Ph)$_2$] (**16**) has a mirror plane bisecting the molecule through palladium and "C–C" bond of carborane.

3. Experimental

The compounds, 1-mercapto-2-phenyl-*o*-carborane (PhCb^{o}SH) [59,60], bis(2-phenyl-*o*-carborane)diselenide, (PhCb^{o}Se)$_2$ [61,62], 1,2-dimercapto-*o*-carborane (HSCb^{o}SH) [63], [MCl$_2$(PR$_3$)$_2$] [64] were prepared according to literature methods. All reactions were carried out in anhydrous conditions under a nitrogen atmosphere. Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out on a Thermo Fisher Flash EA-1112 CHNS instrument. ^{1}H, ^{31}P{^{1}H}, ^{77}Se{^{1}H} and ^{195}Pt{^{1}H} NMR spectra were recorded on a Bruker Avance-II 300 MHz spectrometer operating at 300, 121.5, 57.24 and 64.29 MHz, respectively.

Table 2
The selected bond lengths (Å) and angles (°) for [Pt (SCb^{o}Ph)$_2$(dppm)] (**3**).[a]

Pt1–S1	2.3243 (9)	S1–C1	1.776 (4)
Pt1–S2	2.3799 (9)	S2–C9	1.767 (4)
Pt1–P1	2.2768 (9)	P1–C17	1.858 (4)
Pt1–P2	2.2639 (9)	P2–C17	1.834 (4)
S1–Pt1–S2	80.92 (3)	S2–Pt1–P2	95.03 (3)
P1–Pt1–P2	72.20 (3)	Pt1–P1–C17	92.94 (11)
S1–Pt1–P1	111.33 (3)	Pt1–P2–C17	94.02 (11)
S1–Pt1–P2	172.89 (3)	P1–C17–P2	92.88 (15)
S2–Pt1–P1	166.60 (3)	Pt1–S1–C1	121.07 (12)
		Pt1–S2–C9	108.97 (12)

[a] C–B distances lie between 1.693 (6) and 1.737 (6) Å.

Table 3
The selected bond lengths (Å) and angles (°) for [Pt(SeCb^{o}Ph)$_2$(dppm)] (**5**).[a]

Pt1–Se1	2.4980 (17)	Se1–C2	1.930 (10)
Pt1–Se2	2.4244 (17)	Se2–C10	1.924 (12)
Pt1–P1	2.266 (3)	P1–C1	1.812 (10)
Pt1–P2	2.273 (3)	P2–C1	1.866 (11)
Se1–Pt1–Se2	80.24 (4)	Se2–Pt1–P2	110.05 (8)
P1–Pt1–P2	72.51 (11)	Pt1–P1–C1	94.2 (4)
Se1–-Pt1–P1	96.77 (8)	Pt1–P2–C1	92.5 (3)
Se1–Pt1–P2	168.99 (8)	P1–C1–P2	93.7 (5)
Se2–Pt1–P1	172.02 (8)	Pt1–Se1–C2	105.7 (3)
		Pt1–Se2–C10	119.8 (3)

[a] C–B distances lie between 1.663 (16) and 1.773 (16) Å.

Chemical shifts are relative to internal chloroform peak (7.26 ppm) for ^{1}H and external 85% H_3PO_4 (for ^{31}P), Me_2Se (Ph_2Se_2 in $CDCl_3$, 463 ppm relative to Me_2Se for ^{77}Se) and Na_2PtCl_6 in D_2O (for ^{195}Pt).

3.1. Preparation of [Pd(SCb^{o}Ph)$_2$(dppm)] (**1**)

To a stirred dichloromethane solution (20 ml) of [HSCb^{o}Ph] (105 mg, 0.418 mmol), [PdCl$_2$dppm] (117 mg, 0.208 mmol) and pyridine (34 mg, 0.418 mmol) were added and the whole was stirred for 4 h. The solvent was removed under vacuum and the residue was washed with methanol (2 × 5 ml). Product was recrystallized from CH_2Cl_2/hexane mixture to give a yellow crystalline powder (115 mg, 56% yield); m.p. 198 °C. Anal. Calcd. for $C_{41}H_{52}B_{20}P_2PdS_2$: C, 49.56; H, 5.28%. Found: C, 49.50; H, 5.27%. ^{1}H NMR ($CDCl_3$) δ: 4.13 (t, ^{2}J(P–H) = 10 Hz, PCH_2P); 7.35–7.56 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −42.6 ppm.

3.2. Preparation of [Pd(SCb^{o}Ph)$_2$(dppe)] (**2**)

Prepared similar to **1** using HSCb^{o}Ph (107 mg, 0.42 mmol), [PdCl$_2$dppe] (122 mg, 0.21 mmol) and pyridine (35 mg, 0.44 mmol) in dichloromethane and isolated as an orange crystalline solid in 85% (181 mg) yield, m.p. 160 °C. Anal. Calcd. For $C_{42}H_{54}B_{20}P_2PdS_2.0.5\,(CH_2Cl_2)$: C, 48.61; H, 5.28%. Found: C, 48.11; H, 5.46%; ^{1}H NMR ($CDCl_3$) δ: 2.24–2.37(m, CH_2CH_2); 7.36–7.61 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 54.0 ppm.

3.3. Preparation of [Pt(SCb^{o}Ph)$_2$(dppm)] (**3**)

Prepared similar to **1** using HSCb^{o}Ph (94 mg, 0.37 mmol), [PtCl$_2$dppm] (121 mg, 0.18 mmol) and pyridine (30 mg, 0.38 mmol) in dichloromethane and isolated as a yellow crystalline solid in 52% (105 mg) yield, m.p. 250 °C (single crystals for X-ray analysis were grown from CH_2Cl_2/MeOH/hexane solution). Anal. Calcd. for $C_{41}H_{52}B_{20}P_2PtS_2.CH_2Cl_2$: C, 43.22; H, 4.66%. Found: C, 44.11; H, 4.86%. ^{1}H NMR (C_6D_6) δ: 3.78 (t, ^{2}J(P–H) = 10 Hz; PCH_2P); 6.99–7.09; 7.42–7.47; 7.82–7.85 (m, Ph). ^{31}P{^{1}H} NMR (C_6D_6) δ: −52.6 (^{1}J(Pt–P) = 2605 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −4063 (t, ^{1}J(Pt–P) = 2640 Hz) ppm.

Table 4
The selected bond lengths (Å) and angles (°) for [Pt (SCb^{o}S)(PMe$_2$Ph)$_2$] (**16**).[a]

Pt1–S1	2.3182 (4)	P1–C3	1.8195 (17)
Pt1–P1	2.2741 (4)	P1–C4	1.8169 (16)
S1–C1	1.7828 (15)	P1–C2	1.8160 (16)
C1–C1	1.633 (3)		
S1–Pt1–S2	91.807 (19)	S1A–Pt1–P2	179.354 (14)
P1–Pt1–P2	92.55 (2)	Pt1–S1–C1	105.68 (5)
S1–Pt1–P1	87.824 (15)		

[a] C–B distances lie between 1.711 (2) and 1.733 (2) Å.

Table 5
The selected bond lengths (Å) and angles (°) for [Pt(SCb^{o}S)(PMePh$_2$)$_2$] (**17**).[a]

Pt1–S1	2.3311 (6)	S1–C1	1.783 (2)
Pt1–S2	2.3388 (6)	S2–C2	1.782 (2)
Pt1–P1	2.2735 (6)	C1–C2	1.646 (3)
Pt1–P2	2.2753 (6)		
S1–Pt1–S2	91.55 (2)	S2–Pt1–P1	86.60 (2)
P1–Pt1–P2	94.93 (2)	S2–Pt1–P2	171.34 (2)
S1–Pt1–P1	168.61 (2)	Pt1–S1–C1	104.37 (8)
S1–Pt1–P2	88.58 (2)	Pt1–S2–C2	104.46 (8)

[a] C–B distances lie between 1.717 (4) and 1.736 (4) Å.

3.4. Preparation of [Pd(SeCb^{o}Ph)$_2$(dppe)] (**4**)

To a dichloromethane solution (15 ml) of [PdCl$_2$dppe] (108 mg, 0.188 mmol), a methanolic solution of NaSeCb^{o}Ph (prepared from reduction of (PhCb^{o}Se)$_2$ (112 mg 0.188 mmol) in 5 ml benzene by methanolic solution of NaBH$_4$ (16 mg, 0.42 mmol)) was added with vigorous stirring which continued for 4 h. The solvents were evaporated under vacuum and the residue was extracted with dichloromethane and filtered through a G-3 filtration unit. The filtrate was concentrated under vacuum and the residue was recrystallized from chloroform as a red crystalline solid (155 mg, 75% yield); m.p. 174 °C. Anal. Calcd. for $C_{42}H_{54}B_{20}P_2PdSe_2$: C, 45.80; H, 4.94%. Found: C, 46.79; H, 4.91%. ^{1}H NMR ($CDCl_3$) δ: 2.23–2.28 (m, CH_2P); 7.33–7.82 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 51.8 (^{2}J (Se–P) = 85 Hz); ^{77}Se{^{1}H} NMR ($CDCl_3$) δ: 254 (d, J(Se–P) = 85 Hz) ppm.

3.5. Preparation of [Pt(SeCb^{o}Ph)$_2$(dppm)] (**5**)

Prepared similar to **4** by a reaction between [PtCl$_2$dppm] (143 mg, 0.22 mmol) and NaSeCb^{o}Ph generated *in situ* from (PhCb^{o}Se)$_2$ (131 mg, 0.22 mmol) and methanolic NaBH$_4$ (18 mg, 0.47 mmol) and isolated as a yellow crystalline solid in 62% (159 mg) yield, m.p. 192 °C. Anal. Calcd. for $C_{41}H_{52}B_{20}P_2PtSe_2 \cdot CH_2Cl_2$: C, 40.00; H, 4.32%. Found: C, 40.36; H, 4.29%. ^{1}H NMR (C_6D_6) δ: 3.89 (t, ^{2}J(P–H) = 10 Hz, PCH$_2$P); 4.35 (s, CH_2Cl_2); 7.05–7.06; 7.47–7.52; 7.72–7.75 (m, Ph). ^{31}P{^{1}H} NMR (C_6D_6) δ: −55.7 (^{1}J(Pt–P) = 2649 Hz). ^{77}Se{^{1}H} NMR (C_6D_6) δ: 431(br) ppm. ^{195}Pt{^{1}H} NMR (C_6D_6) δ: −4289 (^{1}J(Pt–P) = 2676 Hz) ppm.

3.6. Preparation of [Pt(SeCb^{o}Ph)$_2$(dppe)] (**6**)

Prepared similar to **4** by a reaction between [PtCl$_2$dppe] (127 mg, 0.19 mmol) and NaSeCb^{o}Ph generated *in situ* from (PhCb^{o}Se)$_2$ (114 mg, 0.22 mmol) and methanolic NaBH$_4$ (17 mg, 0.45 mmol) and isolated as a yellow crystalline solid in 56% (126 mg) yield, m.p. 210 °C. Anal. Calcd. for $C_{42}H_{54}B_{20}P_2PtSe_2$: C, 42.39; H, 4.57%. Found: C, 42.70; H, 4.56%. ^{1}H NMR (C_6D_6) δ: 2.12–2.25 (m, CH_2); 7.32–7.58 (m, Ph). ^{31}P{^{1}H} NMR (C_6D_6) δ: 41.4 (^{1}J(Pt–P) = 2994 Hz). ^{77}Se{^{1}H} NMR (C_6D_6) δ: 266 (d, ^{2}J(Se–P) = 65 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6) δ: −4949 (^{1}J(Pt–P) = 3004 Hz) ppm.

3.7. Preparation of [Pt(SeCb^{o}Ph)$_2$(dppp)] (**7**)

Prepared similar to **4** by a reaction between [PtCl$_2$dppp] (118 mg, 0.17 mmol) and NaSeCb^{o}Ph generated *in situ* from (PhCb^{o}Se)$_2$ (104 mg, 0.17 mmol) and methanolic NaBH$_4$ (15 mg, 0.40 mmol) and isolated as a yellow powder in 53% (111 mg) yield, m.p. 160 °C. Anal. Calcd. for $C_{43}H_{56}B_{20}P_2PtSe_2.CH_2Cl_2$: C, 41.00; H, 4.54%. Found: C, 41.13; H, 4.49%. ^{1}H NMR (C_6D_6) δ: 3.64 (m), 3.87 (m) (CH_2); 6.98–7.16 (m); 7.38 (br), 7.45(br), 7.62 (d, 8 Hz) (Ph). ^{31}P{^{1}H} NMR (C_6D_6) δ: −11.5 (^{1}J(Pt–P) = 2840 Hz) ppm. Because of poor solubility of the complex ^{77}Se and ^{195}Pt NMR spectra could not be obtained.

3.8. Preparation of [Pd(SCb^{o}S)(dppm)] (**8**)

To a stirred dichloromethane solution (20 ml) of [HSCb^{o}SH] (51 mg, 0.245 mmol), [PdCl$_2$dppm] (137 mg, 0.244 mmol) and pyridine (42 mg, 0.531 mmol) were added and the whole was stirred for 4 h. The solvent was removed through vacuum, residue was washed with methanol (2 × 5 ml) and recrystallized from CH_2Cl_2/hexane mixture to give a yellow crystalline powder (91 mg, 53% yield); m.p. 256 °C. Anal. Calcd. for $C_{27}H_{32}B_{10}P_2PdS_2$: C, 46.52; H, 4.63%. Found: C, 46.58; H, 4.43%. ^{1}H NMR ($CDCl_3$) δ: 4.15 (t, J(P–H) = 10 Hz, PCH$_2$P); 7.40–7.52; 7.62–7.68 (m, PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −38.7 ppm.

3.9. Preparation of [Pd(SCb^{o}S)(dppe)] (**9**)

Prepared similar to **8** using HSCb^{o}SH (58 mg, 0.28 mmol) and [PdCl$_2$dppe] (160 mg, 0.28 mmol) and pyridine (50 mg, 0.63 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a yellow crystalline solid (113 mg, 57%), m.p. >300 °C. Anal. Calcd. for $C_{28}H_{34}B_{10}P_2PdS_2$: C, 47.29; H, 4.82%. Found: C, 47.44; H, 4.83%. ^{1}H NMR ($CDCl_3$) δ: 2.36 (d, CH_2–CH_2); 7.46–7.54 (m, PPh$_2$); 7.62–7.67 (m, PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 53.2 ppm.

3.10. Preparation of [Pt(SCb^{o}S)(dppm)] (**10**)

Prepared similar to **8** using HSCb^{o}SH (53 mg, 0.25 mmol) and [PtCl$_2$dppm] (165 mg, 0.25 mmol) and pyridine (48 mg, 0.61 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a white crystalline solid (123 mg, 62%), m.p. >300 °C. Anal. Calcd. for $C_{27}H_{32}B_{10}P_2PtS_2$: C, 41.27; H, 4.10; S, 8.16%. Found: C, 41.59; H, 4.14; S, 8.56%. ^{1}H NMR ($CDCl_3$) δ: 4.44 (t, ^{2}J(P–H) = 10.8 Hz; PCH$_2$P); 7.42–7.51; 7.62–7.68 (m, PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −46.4 (^{1}J(Pt–P) = 2382 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6) δ: −3892 (t, ^{1}J(Pt–P) = 2382 Hz) ppm.

3.11. Preparation of [Pt(SCb^{o}S)(dppe)] (**11**)

Prepared similar to **8** using HSCb^{o}SH (40 mg, 0.19 mmol) and [PtCl$_2$dppe] (128 mg, 0.19 mmol) and pyridine (35 mg, 0.44 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a white crystalline solid (86 mg, 56%), m.p. >300 °C. Anal. Calcd. for $C_{28}H_{34}B_{10}P_2PtS_2$: C, 42.05; H, 4.28%. Found: C, 42.38; H, 4.30%. ^{1}H NMR ($CDCl_3$) δ: 2.25–2.37 (m, CH_2); 7.46–7.51; 7.63–7.67 (m, PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 44.6 (^{1}J(Pt–P) = 2796 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6) δ: −4460 (^{1}J(Pt–P) = 2801 Hz) ppm.

3.12. Preparation of [Pd(SCb^{o}S)(PEt$_3$)$_2$] (**12**)

Prepared similar to **8** using HSCb^{o}SH (65 mg, 0.31 mmol) and [PdCl$_2$(PEt$_3$)$_2$] (129 mg, 0.31 mmol) and pyridine (55 mg, 0.69 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a yellow crystalline solid (89 mg, 52%), m.p. 212 °C. Anal. Calcd. for $C_{14}H_{40}B_{10}P_2PdS_2$: C, 30.62; H, 7.34%. Found: C, 30.81; H, 7.39%. ^{1}H NMR ($CDCl_3$) δ: 1.10–1.18 (m, PCH$_2$Me); 1.75–1.83 (m, PCH$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 19.0 ppm.

3.13. Preparation of [Pd(SCb^{o}S)(PMePh$_2$)$_2$] (**13**)

Prepared similar to **8** using HSCb^{o}SH (44 mg, 0.21 mmol) and [PdCl$_2$(PMePh$_2$)$_2$] (123 mg, 0.21 mmol) and pyridine (36 mg, 0.45 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a yellow crystalline solid (85 mg, 56%), m.p. 252 °C. Anal. Calcd. for $C_{28}H_{36}B_{10}P_2PdS_2$: C, 47.15; H, 5.09%. Found: C, 46.35; H, 5.02%. ^{1}H NMR ($CDCl_3$) δ: 1.59 (d, 8.4 Hz, PMe); 7.29–7.45 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 7.6 ppm.

3.14. Preparation of [Pd(SCb^{o}S)(PPh$_3$)$_2$] (**14**)

Prepared similar to **8** using HSCb^{o}SH (36 mg, 0.17 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (120 mg, 0.17 mmol) and pyridine (30 mg, 0.38 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a yellow crystalline solid (81 mg, 56%), m.p. 260 °C. Anal. Calcd. for $C_{38}H_{40}B_{10}P_2PdS_2$: C, 54.51; H, 4.82%. Found: C, 54.27; H, 4.74%. ^{1}H NMR ($CDCl_3$) δ: 7.18 (t, Ph); 7.34 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 26.0 ppm.

3.15. Preparation of [Pt(SCb^{o}S)(PEt$_3$)$_2$] (**15**)

Prepared similar to **8** using HSCb^{o}SH (63 mg, 0.30 mmol) and [PtCl$_2$(PEt$_3$)$_2$] (153 mg, 0.30 mmol) and pyridine (52 mg, 0.66 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a white crystalline solid (121 mg, 62%), m.p. 213 °C. Anal. Calcd. for $C_{14}H_{40}B_{10}P_2PtS_2$: C, 26.37; H, 6.32%. Found: C, 26.26; H, 6.32%. ^{1}H NMR ($CDCl_3$) δ: 1.06–1.17 (m, PCH_2Me); 1.84–1.97 (m, PCH_2). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 7.6 (^{1}J(Pt–P) = 2775 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −4437 (^{1}J(Pt–P) = 2777 Hz) ppm.

3.16. Preparation of [Pt(SCb^{o}S)(PMe$_2$Ph)$_2$] (**16**)

Prepared similar to **8** using HSCb^{o}SH (53 mg, 0.25 mmol) and [PtCl$_2$(PMe$_2$Ph)$_2$] (103 mg, 0.25 mmol) and pyridine (45 mg, 0.57 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield a white crystalline solid (88 mg, 51%), m.p. 275 °C. Anal. Calcd. for $C_{18}H_{32}B_{10}P_2PtS_2$: C, 31.90; H, 4.76%. Found: C, 31.91; H, 4.72%. ^{1}H NMR ($CDCl_3$) δ: 1.53 (d, ^{2}J(P–H) = 10 Hz, J(Pt–H) = 27 Hz; PMe_2); 7.32–7.35; 7.40–7.45 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −17.6 (^{1}J(Pt–P) = 2784 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6) δ: −4358 (^{1}J(Pt–P) = 2803 Hz) ppm.

3.17. Preparation of [Pt(SCb^{o}S)(PMePh$_2$)$_2$] (**17**)

Prepared similar to **8** using HSCb^{o}SH (31 mg, 0.15 mmol) and [PtCl$_2$(PMePh$_2$)$_2$] (99 mg, 0.15 mmol) and pyridine (28 mg, 0.35 mmol) and recrystallized from CH_2Cl_2/hexane mixture to yield an off-white crystalline solid (71 mg, 60%), m.p. 250 °C. Anal. Calcd. for $C_{28}H_{36}B_{10}P_2PtS_2$: C, 41.94; H, 4.52%. Found: C, 41.23; H, 4.46%. ^{1}H NMR ($CDCl_3$) δ: 1.73 (d, J(P–H) = 9.5 Hz; J(Pt–H) = 36 Hz, PMe); 7.27–7.31; 7.37–7.42 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −1.5 (^{1}J(Pt–P) = 2848 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6) δ: −4381 (^{1}J(Pt–P) = 2859 Hz) ppm.

3.18. Preparation of [Pt(SCb^{o}Ph)$_2$(PMe$_2$Ph)$_2$] (**18**)

Prepared similar to **1** using HSCb°Ph (83 mg, 0.33 mmol), [PtCl$_2$(PMe$_2$Ph)$_2$] (89 mg, 0.16 mmol) and pyridine (30 mg, 0.38 mmol) in dichloromethane and isolated as an off-white crystalline solid in 62% (99 mg) yield, m.p. 215 °C. Anal. Calcd. for $C_{32}H_{52}B_{20}P_2PtS_2$: C, 39.46; H, 5.38%. Found: C, 39.73; H, 5.40%. ^{1}H NMR ($CDCl_3$) δ: 1.14, 1.27 (br, each singlet, PMe_2) 7.09–7.76 (m, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −16.3 (^{1}J (Pt–P) = 3031 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −4572 (^{1}J(Pt–P) = 3033 Hz) ppm.

3.19. Crystallographic experiments

Single crystal X-ray diffraction data for [Pt(SCb^{o}Ph)$_2$(dppm)], [Pt(SeCb^{o}Ph)$_2$(dppm)], [Pt(SCb^{o}S)(PMe$_2$Ph)$_2$] and [Pt(SCb^{o}S)(PMePh$_2$)$_2$] were collected on a Bruker APEX 2 CCD diffractometer

Table 6
Crystallographic and structure refinement data for [Pt (SCb^{o}Ph)$_2$(dppm)] (**3**), [Pt(SeCb^{o}Ph)$_2$(dppm)] (**5**), [Pt (SCb^{o}S)(PMe$_2$Ph)$_2$] (**16**) and [Pt(SCb^{o}S)(PMePh$_2$)$_2$] (**17**).

	[Pt (SCb^{o}Ph)$_2$(dppm)] (**3**)	[Pt(SeCb^{o}Ph)$_2$(dppm)] (**5**)	[Pt (SCb^{o}S)(PMe$_2$Ph)$_2$] (**16**)	[Pt(SCb^{o}S)(PMePh$_2$)$_2$] (**17**)
Chemical formula	$C_{41}H_{52}B_{20}P_2PtS_2.CH_2Cl_2$, 0.75($CH_3OH$), 0.25($C_6H_{14}$)	$C_{41}H_{52}B_{20}P_2PtSe_2.CH_2Cl_2$	$C_{18}H_{32}B_{10}P_2PtS_2$	$C_{28}H_{36}B_{10}P_2PtS_2.0.5(CH_2Cl_2)$
Formula weight	1212.68	1260.90	677.69	844.28
T/K	100 (2)	120 (2)	100 (2)	100 (2)
Size/color	0.25 × 0.13 × 0.10/ colourless-plate	0.35 × 0.25 × 0.20/ colourless-needle	0.42 × 0.23 × 0.20/ colourless-needle	0.45 × 0.30 × 0.25/ colourless-plate
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_{1/c}$	P-1	C 2/c	P $2_{1/n}$
a/Å	12.1658 (6)	12.018 (6)	17.0781 (5)	11.9632 (5)
b/Å	23.2493 (11)	13.868 (7)	12.7838 (4)	20.4256 (8)
c/Å	19.8148 (9)	17.965 (11)	12.2130 (4)	15.2455 (6)
α/°	90.00	67.441(13)	90.00	90.00
β/°	104.2720 (10)	83.248 (18)	97.3730 (10)	110.4120 (10)
γ/°	90.00	70.569 (12)	90.00	90.00
V/Å^3	5431.6 (4)	2607 (2)	2644.33 (14)	3491.4 (2)
Z	4	2	4	4
d_{calc}/g cm^{-3}	1.483	1.606	1.702	1.606
μ (mm^{-1})/F(000)	2.853/2424	4.283/1232	5.593/1320	4.328/1660
θ for data collection	1.94–29.00	2.05–26.00	2.41–29.99	2.45–29.00
Limiting indices	$-16 \le h \le 16$ $-31 \le k \le 31$ $-26 \le l \le 27$	$-14 \le h \le 14$ $-17 \le k \le 17$ $-22 \le l \le 22$	$-24 \le h \le 24$ $-17 \le k \le 17$ $-17 \le l \le 17$	$-16 \le h \le 16$ $-27 \le k \le 27$ $-20 \le l \le 16$
No. of reflections collected	14,386	10,121	16,520	28,142
No. of observed reflections with $I > 2\sigma(I)$	10,692	5219	3721	8030
Data/restraints/parameters	14,386/5/660	10,121/0/626	3833/0/152	9227/0/415
Final R_1, ωR_2 indices (R_factor_gt/ωR_factor_gt)	0.0436/0.0835	0.0687/0.1069	0.0143/0.0348	0.0226/0.0516
R_1, ωR_2 (all data) (R_factor_all/ωR_Factor_ref)	0.0700/0.0939	0.1454/0.1284	0.0151/0.0351	0.0301/0.0516
GOF	1.004	1.028	1.007	1.015
Largest difference peak and hole (e Å^{-3})	2.481 and −1.169	2.113 and −0.978	1.141 and −0.670	1.209 and −0.926

using graphite monochromated Mo Kα radiation ($\lambda = 0.71703$ Å). Low temperature of the crystals was maintained with a cryostream (Oxford Cryo-system) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software and semi-empirical method SADABS [65,66]. The structures were solved by direct methods [67] and refinement was on F^2 using data that had been corrected for Lorentz and polarization effects with an empirical procedure [68]. The non-hydrogen atoms were refined anisotropically. All carborane hydrogen atoms were located from difference Fourier synthesis, the H(C) atoms were placed in geometrically calculated positions. All hydrogen atom positions were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 Ueq(Xi) or Ueq(Ci) where U(Xi) are the equivalent thermal parameters of the boron and methylene carbon. Molecular structures were drawn using ORTEP [69]. Crystallographic data, together with the data collection and refinement details are given in Table 6.

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Appendix A. Supplementary data

CCDC Nos. 833858 (for **3**), 833857 (for **5**), 833859 (for **16**) and 833860 (for **17**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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. E-mail: deposit@ccdc.cam.ac.uk].

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