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# Synthesis, spectroscopy and structures of palladium(II) and platinum(II) complexes containing mercapto-*o*-carborane

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ABSTRACT

The reactions of $[M_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with mercapto-*o*-carboranes in the presence of pyridine afforded mono-nuclear complexes of composition, [MCl(SCb°R)(py)($PMe_2Ph$)] (M = Pd or Pt; Cb° = *o*-$C_2B_{10}H_{10}$; R = H or Ph). The treatment of $[PdCl_2(PEt_3)_2]$ with PhCb°SH yielded *trans*-$[Pd(SCb°Ph)_2(PEt_3)_2]$ (**4**) which when left in solution in the presence of pyridine gave another substitution product, $[Pd(SCb°Ph)_2(py)(PEt_3)]$ (**5**). The structures of [PdCl(SCb°Ph)(py)($PMe_2Ph$)] (**1**), $[Pd(SCb°Ph)_2(PEt_3)_2]$ (**4**) and $[Pd(SCb°Ph)_2(py)(PEt_3)]$ (**5**) were established unambiguously by X-ray crystallography. The palladium atom in these complexes adopts a distorted square-planar configuration with neutral donor atoms occupying the *trans* positions. Thermolysis of [PdCl(SCb°)(py)($PMe_2Ph$)] (**2**) in TOPO (trioctylphosphine oxide) at 200 °C gave nanocrystals of TOPO capped $Pd_4S$ which were characterized by XRD pattern and SEM.



## 1. Introduction

Palladium and platinum chalcogenolate complexes have attracted considerable attention for quite sometime owing to their diverse structural features [1–4], photo-physical properties [5] and applications in catalysis [6,7] and materials science [8,9]. Simple chalcogenolates usually afford polymeric insoluble complexes limiting their utility as molecular precursors. To suppress polymerization a number of strategies have been adopted. These include use of ancillary ligands on metal [10,11], internal functionalization of organochalcogen ligand [12] and sterically demanding ligand [2,13,14]. The latter strategy suffers from the excessive presence of carbon which may get incorporated in metal chalcogenide. Thus ligands containing trimethylsilyl fragments were developed [15,16]. Another interesting families of ligands incorporating *o*-carboranes may be conceived which would not only impose a three dimensional steric demand but also give cleaner depositions due to a weaker C–S linkage. Such ligands, *e.g.*, 1-mercapto-2-phenyl-*o*-carborane [17,18], have been known in the literature for quite some time now [19,20]. Thus in pursuance of our interest on palladium and platinum complexes with organochalcogenolates, we have examined a few reactions of 1-mercapto-2-phenyl-*o*-carborane and mercapto-*o*-carborane with palladium and platinum complexes and evaluated the suitability of one representative compound for the preparation of palladium sulfide nanocrystals. The results of this work are reported herein.

## 2. Experimental

All experiments were carried out under anhydrous conditions in an inert atmosphere. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance-II 300 MHz NMR spectrometer. X-ray powder diffraction data were collected on a Philips X-ray diffractometer (Model PW 1729) using Cu Kα radiation. SEM (scanning electron microscopy) and EDAX (energy dispersive X-ray analysis) measurements were made on a MIRERO AIS-2100 and OXFORD INCA E-350 instrument, respectively. The compounds 1-mercapto-*o*-carborane (Cb°SH) [19], 1-mercapto-2-phenyl-*o*-carborane (PhCb°SH) [17,18], $[M_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ [21] and $[PdCl_2(PEt_3)_2]$ were prepared according to the literature methods.

### 2.1. [PdCl(SCb°Ph)(py)($PMe_2Ph$)] (*1*)

To a stirred dichloromethane solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (57 mg, 0.09 mmol), PhCb°SH (45 mg, 0.18 mmol) and three drops of pyridine were added and the whole was stirred for additional 4 h. Addition of diethylether led to precipitation of py·HCl which was filtered off and the filtrate was concentrated *in vacuo*. The

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residue was recrystallized from $CH_2Cl_2$–$Et_2O$ in 62% yield; m.p. 127 °C (decomp.). Anal. Calcd. for $C_{21}H_{31}B_{10}ClNPSPd$: C, 41.3; H, 5.1; N, 2.3; Cl, 5.8%. Found: C, 41.4; H, 4.8; N, 2.3; Cl, 6.2%. $^1H$ NMR in $CDCl_3$: 1.70 (d, 12.0 Hz, PMe); 7.31–7.79 (10H, Ph); 8.76 (br, py): $^{31}P\{^1H\}$ NMR in $CDCl_3$ $\delta$: 5.4 ppm.

### 2.2. [PdCl(SCb°)(py)(PMe$_2$Ph)] (**2**)

Prepared similar to **1** using $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (112 mg, 0.18 mmol) and Cb°SH (62 mg, 0.35 mmol) in 74% yield, m.p., 47 °C. Anal. Calcd. for $C_{15}H_{27}B_{10}ClNPSPd$: C, 33.7; H, 5.1; N, 2.6%. Found: C, 32.9; H, 4.3; N, 2.6%. $^1H$ NMR in $CDCl_3$: 1.90 (d, 11.6 Hz, PMe); 7.50–7.81 (5H, Ph); 8.97 (m, py). $^{31}P\{^1H\}$ NMR in $CDCl_3$ $\delta$: 4.7 ppm.

### 2.3. [PtCl(SCb°Ph)(py)(PMe$_2$Ph)] (**3**)

Prepared similar to **1** using $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (70 mg, 0.09 mmol) and PhCb°SH (44 mg, 0.17 mmol) in 55% yield, m.p., 85 °C. Anal. Calcd. for $C_{21}H_{31}B_{10}ClNPSPt$: C, 36.1; H, 4.5; N, 2.0%. Found: C, 35.1; H, 3.7; N, 2.4%. $^1H$ NMR in $CDCl_3$ : 1.63 (s, PMe) 7.24–7.93 (10H, Ph), 8.75–8.91 (5H, py). $^{31}P\{^1H\}$ NMR in $CDCl_3$ $\delta$: −21.3 ($^1J(^{195}Pt–^{31}P)$ = 3506 Hz) ppm.

### 2.4. [Pd(SCb°Ph)$_2$(PEt$_3$)$_2$] (**4**)

Prepared similar to **1** using $[PdCl_2(PEt_3)_2]$ (58 mg, 0.14 mmol) and PhCb°SH (49 mg, 0.20 mmol) in 30% yield, m.p. 145 °C (decomp.). Anal. Calcd. for $C_{28}H_{60}B_{20}P_2S_2Pd$: C, 39.8; H, 7.1%. Found: C, 39.0; H, 7.2%. $^1H$ NMR in $CDCl_3$: 0.87 (q, 8.0 Hz, $-CH_2$); 1.55 (t, 4 Hz, $-CH_3$); 7.3–7.7 (5H, Ph); $^{31}P\{^1H\}$ NMR in $CDCl_3$ $\delta$: 4.3.ppm.

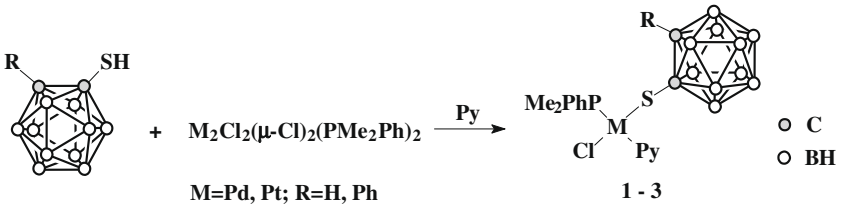
When a dichloromethane solution of **4** containing a few drops of pyridine was left for several hours a substitution complex, [Pd(SCb°Ph)$_2$(py)(PEt$_3$)] (**5**) was isolated, m.p., 95 °C. Anal. Calcd. for $C_{27}H_{50}B_{20}NPS_2Pd$: C, 40.2; H, 6.2; N, 1.7%. Found: C, 40.6; H, 5.8; N, 1.8%. $^1H$ NMR in $CDCl_3$: 0.95 (m, $PCH_2CH_3$), 1.69 (m, $PCH_2$), 7.33–7.49 (m, Ph + py);, 8.72 (d, 5.2 Hz, py); $^{31}P\{^1H\}$ NMR in $CDCl_3$ $\delta$: 28.7 ppm.

### 2.5. Thermolysis of [PdCl(SCb°)(py)(PMe$_2$Ph)] (**2**)

TOPO (trioctylphosphine oxide) (2.5 g) was heated in a three necked flask up to 200 °C under a nitrogen atmosphere. To this hot stirring liquid, a dichloromethane (2 ml) solution of **2** (116 mg) was injected using a syringe. The whole was kept at 200 °C with stirring for 3 h. After cooling to room temperature, the contents were centrifuged leaving a black residue which was washed with methanol (10 ml × 3) and dried *in vacuo*.

**Table 1**
Crystallographic and structure refinement data for [PdCl(SCb°Ph)(py)(PMe$_2$Ph)] 0.2($C_3H_6O$) (**1a**), [Pd(SCb°Ph)$_2$(PEt$_3$)$_2$] (**4**) and [Pd(SCb°Ph)$_2$(py)(PEt$_3$)] (**5**).

| Complex | **1a** | **4** | **5** |
|---|---|---|---|
| Chemical formula | $C_{21}H_{31}B_{10}Cl_1N_1P_1Pd_1S_1$ | $C_{28}H_{60}B_{20}P_2Pd_1S_2$ | $C_{27}H_{50}B_{20}N_1P_1Pd_1S_2$ |
| Formula wt. | 610.37 | 845.32 | 806.23 |
| Color | Yellow | Red | Yellow |
| Crystal size ($mm^3$) | 0.45 × 0.35 × 0.20 | 0.40 × 0.35 × 0.20 | 0.1 × 0.4 × 0.4 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ | $P2_1/n$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 17.326(2) | 13.926(9) | 22.000(6) |
| $b$ (Å) | 10.773(1) | 16.158(1) | 11.826(6) |
| $c$ (Å) | 16.136(2) | 19.972(1) | 18.420(6) |
| $\beta$ (°) | 100.543(2) | 102.440(1) | 101.03(2) |
| $V$ (Å$^3$) | 2820.3(5) | 4388.7(5) | 4704(3) |
| $Z$ | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.438 | 1.280 | 1.139 |
| Diffractometer | Bruker SMART | Bruker APEX 2 | Rigaku AFC7S |
| $T$, K | 120 | 100 | 298 |
| $2\theta_{max}$ (°) | 54 | 54 | 55 |
| Absolute coefficient, $\mu$ (Mo K$\alpha$) (cm$^{-1}$) | 5.61 | 6.14 | 0.538 |
| Absorption correction | SADABS | SADABS | Psi-scans |
| $T_{max}$ and $T_{min}$ | 0.695 and 0.561 | 0.658 and 0.730 | 0.900 and 0.8135 |
| No. of reflections collected | 25 293 | 24 428 | 12 978 |
| No. of unique reflections collected ($R_{int}$) | 6073 (0.0522) | 4860 (0.0307) | 10 884 (0.0587) |
| No. of observed reflection ($I > 2\sigma(I)$) | 2327 | 2284 | 6534 |
| No. of parameters | 327 | 294 | 469 |
| $R_1$ (on $F$ for obs. reflections) | 0.482 | 0.0230 | 0.590 |
| $wR_2$ (on $F^2$ for all reflection) | 0.1083 | 0.0620 | 0.1218 |
| GOF | 1.077 | 1.014 | 1.060 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.126 and −0.523 | 0.055 and 0.337 | 1.0300 and −0.7800 |




**Scheme 1.**

### 2.6. Crystallography experiment

Single-crystal X-ray diffraction experiments were carried on Bruker SMART 1000 CCD, Bruker APEX 2 and Rigaku AFC7S diffractometers for **1**, **4** and **5**, respectively, using graphite monochromated Mo K radiation ($\lambda$ = 0.71073 Å). Low temperature of the crystals was maintained with a Cryostream (Oxford Cryo-systems) open-flow $N_2$ gas cryostat. Reflection intensities were integrated using SAINT software and semi-empirical method SADABS [22,23]. The structures were solved by direct methods [24], and refinement was on $F^2$ [25] using data corrected for absorption correction effects with an empirical procedure [26,27]. The non-hydrogen atoms were refined with anisotropic displacement parameters. All carborane hydrogen atoms in **1a** and **4** were located from the difference Fourier syntheses, the H(C) atoms were placed in geometrically calculated positions. All hydrogen carbon atom positions in **1a** and **4** and carborane hydrogen atom positions in **1a** were refined in isotropic approximation using riding model with the $U_{iso}$(H) parameters equal to 1.2 $U_{eq}$(Xi) or $U_{eq}$(Ci), where $U$(Xi) are the equivalent thermal parameters of the boron and methyne carbon. The carborane hydrogen atom positions for **4** were refined in isotropic approximation. All hydrogen atoms in **5** were placed in calculated positions and refined in isotropic approximation using riding model. All calculations were performed on an IBM PC/AT using the SHELXTL software [25]. Molecular structure was drawn using ORTEP [28]. Crystallographic data and structural refinement details are given in Table 1.

## 3. Results and discussion

Treatment of $[M_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with two mole equivalents of mercapto-*o*-carboranes in the presence of pyridine as HCl scavenger afforded mono-nuclear complexes, $[MCl(SCb^oR)(py)(PMe_2Ph)]$ (M = Pd or Pt; R = H or Ph) rather than the expected thiolato-bridged binuclear derivatives, $[M_2Cl_2(\mu\text{-}SCb^oR)_2(PMe_2Ph)_2]$ (Scheme 1).

It is noteworthy that the binuclear complexes $[M_2Cl_2(\mu\text{-}SR)_2(PMe_2Ph)_2]$ (M = Pd or Pt) are inert to bridge cleavage reactions by ligands like pyridine [29]. The steric bulk of carborane in the present case seems to facilitate the formation of mono-nuclear products which are interesting examples of square-planar complexes containing four different ligands. In the $^1$H NMR spectra of these complexes the SH proton resonance was absent indicative of deprotonation of the ligand. The spectra exhibited expected resonances. The $^{31}P\{^1H\}$ NMR spectra showed a single resonance suggesting the formation of only one isomeric species.

A freshly prepared $CDCl_3$ solution of the platinum complex (**3**) exhibited a single resonance with $^1J$(Pt–P) of 3506 Hz. The complex slowly isomerized in solution to another species in which phosphine is trans to pyridyl nitrogen ($\delta$ $^{31}$P: −20.4 ($^1J$(Pt–P) = 3528 Hz). The two species existed in 1:1 ratio (Scheme 2).

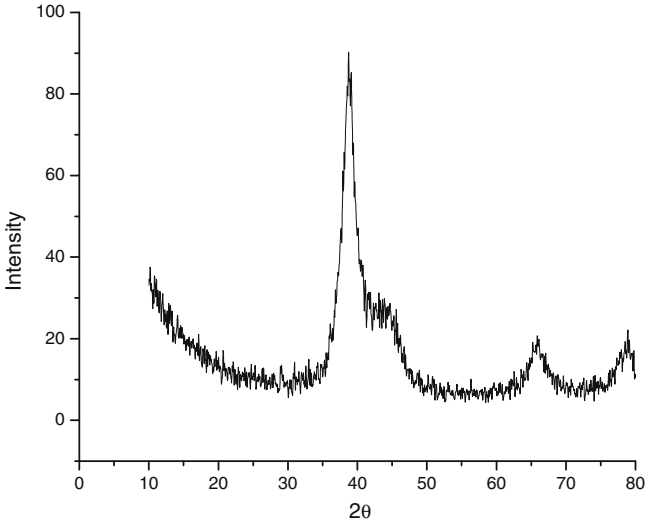



**Fig. 1.** XRD pattern of $Pd_4S$ obtained from thermolysis of $[PdCl(SCb^o)(py)(PMe_2Ph)]$ (**2**) in TOPO at 200 °C.

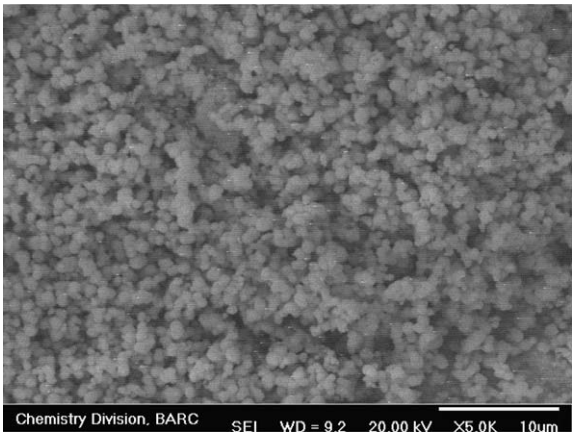
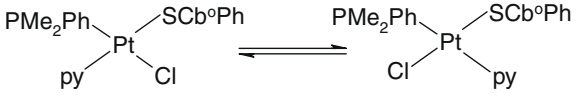
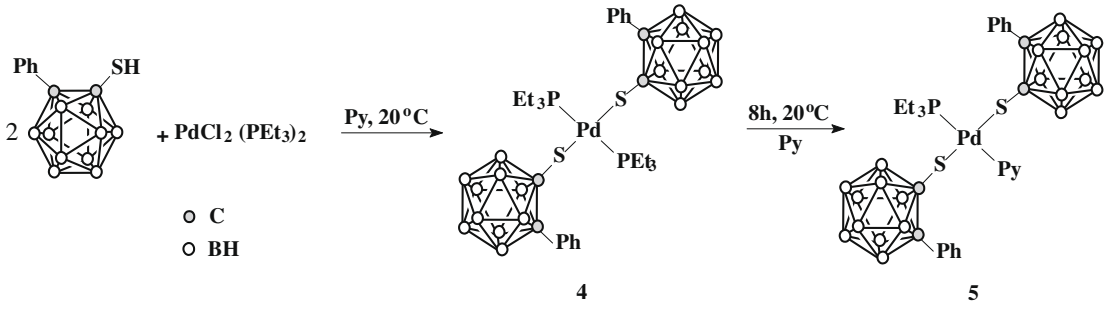



**Fig. 2.** SEM micrograph of $Pd_4S$ obtained from thermolysis of $[PdCl(SCb^o)(py)(PMe_2Ph)]$ (**2**) in TOPO at 200 °C.




**Scheme 2.**




**Scheme 3.**

Reaction of $[PdCl_2(PEt_3)_2]$ with PhCb°SH in the presence of pyridine yielded initially *trans*-$[Pd(SCb°Ph)_2(PEt_3)_2]$ (**4**) ($\delta$ $^{31}$P: 4.3 ppm). When the solution was left for several hours at room temperature, yellow crystals of $[Pd(SCb°Ph)_2(py)(PEt_3)]$ (**5**) were formed by substitution of one triethyl phosphine ligand by pyridine. It is rather unusual in a sense the strong binding phosphine ligand is replaced by pyridine (Scheme 3).

To access the suitability of these complexes for the preparation palladium sulfide nanocrystals, thermolysis of one representative complex **2** was carried out in TOPO (trioctylphosphine oxide). The complex **2** on thermolysis at 200 °C gave a black residue of TOPO capped $Pd_4S$ as revealed by EDAX (Calcd for $Pd_4S$: Pd, 93.0; S, 7.0; Found: Pd, 92.2; S, 4.7; P, 1.15%) and XRD pattern (Fig. 1) (JCPDS File No 10-335). The SEM micrograph (Fig. 2) showed that the particles are spherical in shape with an average diameter of ~100 nm. Extrusion of carborane in metal complexes has been reported recently to give metal nanoparticles [30]. For example, the complex $[IrH(7,8\text{-nido-}C_2B_9H_{11})(PPh_3)_2]$ in ethylene glycol under hydrogen atmosphere at 160 °C yields iridium nanoparticles [30].

**Table 2**
The selected bond lengths (Å) and angles (°) for **1**, **4** and **5**.

| | [PdCl(SCb°Ph)(py)($PMe_2Ph$)] (**1**) | [$Pd(SCb°Ph)_2(PEt_3)_2$] (**4**) | [$Pd(SCb°Ph)_2(py)(PEt_3)$] (**5**) |
|---|---|---|---|
| Pd–S | 2.302(1) | 2.3595(4) | 2.3168(15), 2.3380(16) |
| Pd–P | 2.243(1) | 2.3582(4) | 2.2564(16) |
| Pd–Cl | 2.342(1) | | |
| Pd–N | 2.141(3) | | 2.117(5) |
| ΔPd (Å) | 0.059 | 0.212 | |
| S–$C_1$(cb) | 1.781(4) | 1.768(1) | 1.763(6), 1.795(6) |
| $C_1$(cb)–$C_2$(cb) | 1.759(6) | 1.777(2) | 1.751(8), 1.741(8) |
| $C_2$(cb)–C(Ph) | 1.499(5) | 1.503(2) | 1.510(9), 1.500(8) |
| $C_1$(cb)–B(3) | 1.719(6) | 1.731(2) | 1.728(9) |
| $C_1$(cb)–B(4) | 1.709(6) | 1.710(2) | 1.720(9) |
| $C_1$(cb)–B(5) | 1.698(6) | 1.706(2) | 1.725(9) |
| $C_1$(cb)–B(6) | 1.741(6) | 1.737(2) | 1.744(9) |
| $C_2$(cb)–B(3) | 1.738(6) | 1.733(2) | 1.719(10) |
| $C_2$(cb)–B(6) | 1.724(6) | 1.720(2) | 1.726(9) |
| $C_2$(cb)–B(7) | 1.715(6) | 1.701(2) | 1.672(10) |
| $C_2$(cb)–B(11) | 1.719(6) | 1.703(2) | 1.711(9) |

| 1 | | 4 | | 5 | |
|---|---|---|---|---|---|
| S–Pd–Cl | 177.41(4) | S–Pd–S′ | 179.62(2) | S1–Pd–S2 | 177.000(5) |
| S–Pd–P | 90.41(4) | P–Pd–P1′ | 158.91(2) | S1–Pd–P | 91.26(6) |
| S–Pd–N | 90.92(10) | P–Pd–S | 89.16(1) | S2–Pd–P | 86.00(6) |
| Cl–Pd–N | 88.19(10) | | | N–Pd–S1 | 91.25(13) |
| N–Pd–P | 176.19(9) | | | N–Pd–S2 | 91.54 (14) |
| | | | | N–Pd–P | 176.20(15) |

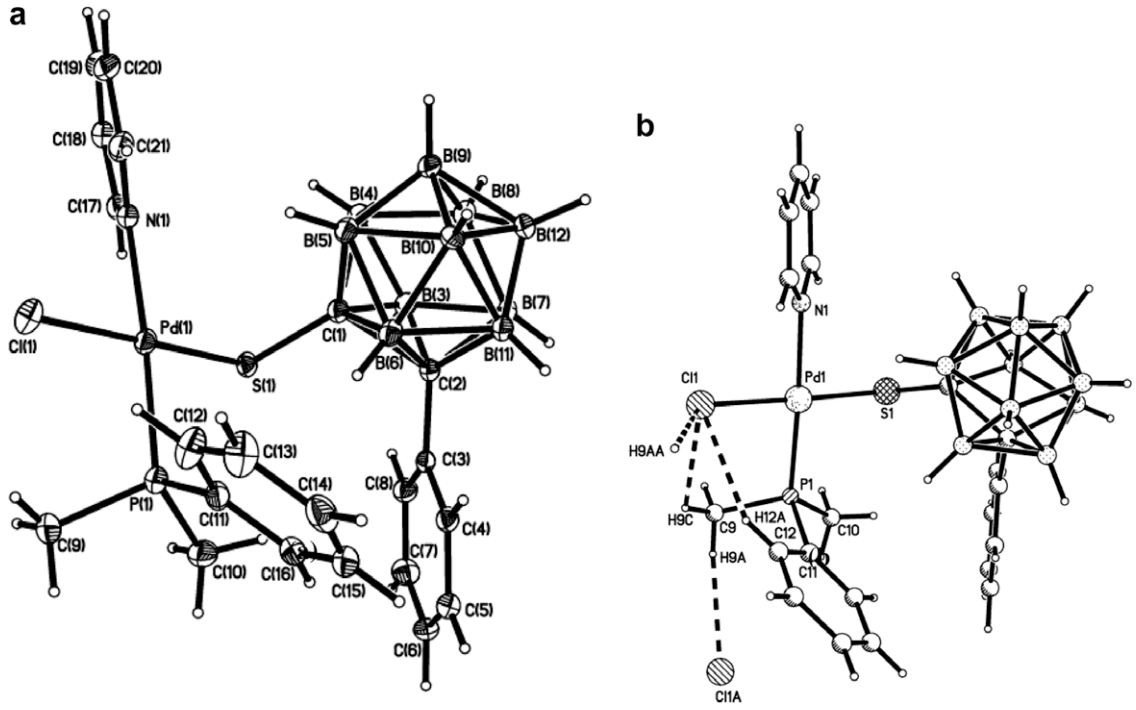



**Fig. 3.** (a) Molecular structure of [PdCl(SCb°Ph)(py)($PMe_2Ph$)] (**1**) drawn with 50% probability; (b) Inter- and intra-molecular hydrogen bond in **1a** (the distances Cl(1)···H(9c), Cl(1)···H(12a) and Cl(1)···H(9aa) 2.71, 2.75, and 2.64 Å, respectively, the bond angles Cl(1)–H–C equal to 117°, 145° and 156°, respectively).

## 4. Molecular structures of [PdCl(SCb°Ph)(py)(PMe$_2$Ph)] (1), [Pd(SCb°Ph)$_2$(PEt$_3$)$_2$] (4) and [Pd(SCb°Ph)$_2$(py)(PEt$_3$)] (5)

Molecular structures of **1**, **4** and **5** have been established unambiguously by X-ray crystallography. Selected bond lengths and angles are given in Table 2 and ORTEP drawings with crystallographic numbering schemes are shown in Figs. 3–5. The palladium atoms in these complexes adopt a distorted square-planar configuration defined by "ClNPS", "$S_2P_2$" and $S_2$NP" donor sets in **1**, **4** and **5,** respectively. The neutral donors in these complexes occupy mutually *trans* positions.

*Trans* influence of various donor atoms around palladium was reflected in their bond distances involving palladium atom. Thus Pd–S distance in **1** is slightly shorter than those observed in **4** and **5**, due to weak *trans* influence of the chloride ion, although the Pd–S distances in all these complexes are within the range reported for palladium thiolates [9,11,31]. Similarly the Pd–P distances in **1** and **5** are shorter by ~0.1 Å than **4** owing to the strong *trans* influence of the phosphine in the latter. The C–S distances in all these complexes vary between 1.763(6) and 1.795 (6) Å, which can be compared with those reported in Cb°–SH (1.776 Å) and Cb°–SPh (1.784 Å) [32,33]. The C–C bond length in carboranes is sensitive to the nature of attached sulfur atom. The C–C distances in Cb°–SH, Cb°–SPh and Cb°–S$^-$ are 1.720, 1.708 and 1.836 Å, respectively [32–34]. The C–C distances in our complexes lie in the range 1.741(8)–1.777(2) Å which are slightly shorter than the one reported in Cb°–S$^-$ anion.

The steric demand of three dimensional carborane fragment is reflected on various angles around palladium atom. The P–Pd–P angle in **4** has been reduced significantly (158.91°) from the ideal value of 180°. When one of the phosphines is replaced by a less bulky pyridine ligand as in **1** and **5**, the P–Pd–N (angles involving neutral donors) is opened up (~176°). The angles S–Pd–E (E = Cl or S) (177.0–179.6°) are closed to ideal value of 180°.

In **1** there are weak interaction between Cl and one of the hydrogen atoms of the methyl group of PMe$_2$Ph (Fig. 1b) as Cl···H

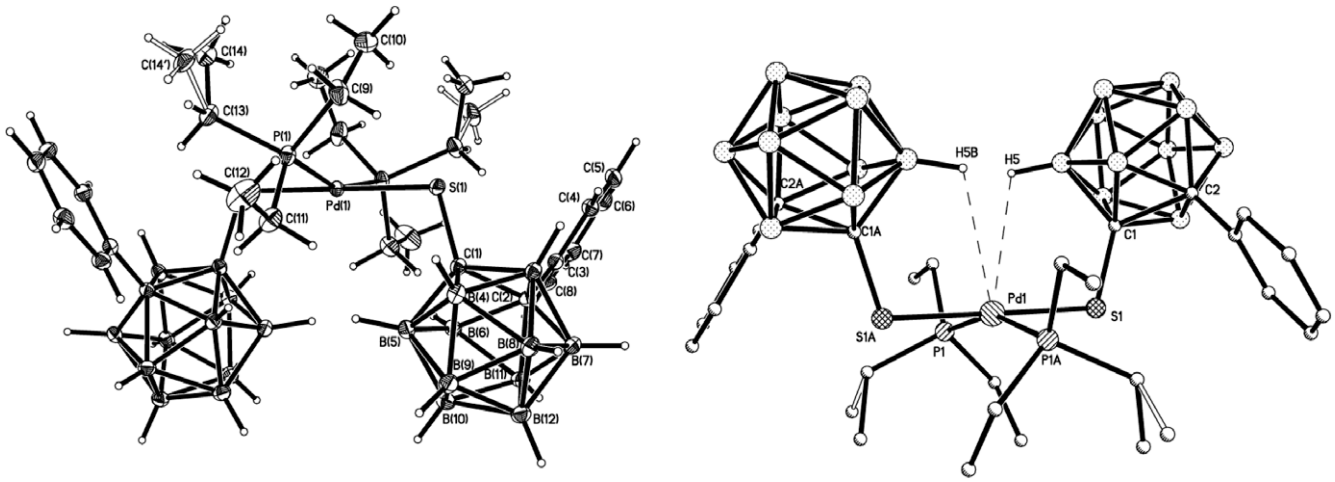



**Fig. 4.** (a) Molecular structure of [Pd(SCb°Ph)$_2$(PEt$_3$)$_2$] (**4**) drawn with 50% probability; (b) intra-molecular interactions between Pd atom and hydrogen atoms of carborane in **4**.

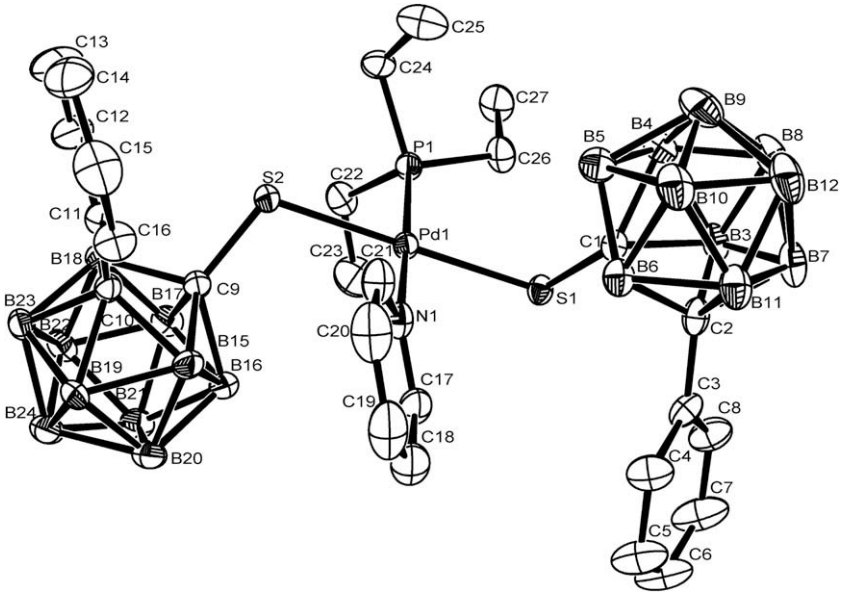



**Fig. 5.** Molecular structure of [Pd(SCb°Ph)$_2$(py)(PEt$_3$)] (**5**) drawn with 50% probability.

distances are shorter than the sum of van-der-Waals radii [35]. Similarly in **4** weak Pd···H (2.32 Å) interaction can be noted (Fig. 4 b).

## Acknowledgements

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## Appendix A. Supplementary data

CCDC 701528, 701529 and 713153 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.014.

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