# Three monoalkoxy-substituted *nido*-platinaboranes: [(PPh₃)₂PtB₁₀H₁₁-8-(OCH₃)], [(PPh₃)₂PtB₁₀H₁₁-8-{OCH-(CH₃)₂}] and [(PPh₃)₂PtB₁₀H₁₀-9-{OCH(CH₃)₂}]

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Each of the title compounds, 8-methoxy-7,7-bis(triphenyl-phosphine-*P*)-8,9:10,11-di-*μH*-7-platina-*nido*-undecaborane dichloromethane hemisolvate, [Pt(CH₁₄B₁₀O)(C₁₈H₁₅P)₂]·· 0.5CH₂Cl₂, (I), 8-isopropoxy-7,7-bis(triphenylphosphine-*P*)-8,9:10,11-di-*μH*-7-platina-*nido*-undecaborane dichloromethane solvate, [Pt(C₃H₁₈B₁₀O)(C₁₈H₁₅P)₂]·CH₂Cl₂, (II), and 9-isopropoxy-7,7-bis(triphenylphosphine-*P*)-8,9:10,11-di-*μH*-7-platina-*nido*-undecaborane dichloromethane solvate, [Pt(C₃H₁₈B₁₀O)(C₁₈H₁₅P)₂]·CH₂Cl₂, (III), has an 11-vertex *nido* polyhedral skeleton, with the 7-platinum centre ligating to two *exo*-polyhedral PPh₃ groups and an alkoxy-substituted polyhedral borane ligand. Compounds (II) and (III) are isomers. The Pt—B distances are in the range 2.214 (7)–2.303 (7) Å for (I), 2.178 (16)–2.326 (16) Å for (II) and 2.205 (6)–2.327 (6) Å for (III).

## Comment

The polyhedral borane dianion $B_{10}H_{10}^{2-}$ has been extensively studied due to its extreme thermal, hydrolytic and oxidative stability (Mutterties & Knoth, 1968; Kennedy, 1986; Barton & Srivastava, 1995). Although a number of metal derivatives have been prepared, little work has been reported on the cage-opening mechanism. Marshall *et al.* (1967) postulated the cage opening of $B_{10}H_{10}^{2-}$ in the anhydrous HCl/diethyl sulfide system as occurring *via* a two-proton attack process on two pairs of apex-to-equatorial B atoms. Paxson & Hawthorne (1975) studied the reaction of PtCl₂(PPh₃)₂ and K₂B₁₀H₁₀ in alcoholic chloroform, and obtained the alkoxy-substituted *nido*-[(PPh₃)₂PtB₁₀H₁₁(OC₂H₅)]; spectroscopic studies showed that the ethoxy group could be at various positions

(*i.e.* 2, 3, 8, 9, 10 or 11). Gaft *et al.* (1983) found that the hydrogen-bridged compound [(PPh₃)₂PtB₁₀H₁₀], derived from the reaction of PtI₂(PPh₃)₂ and Ag₂B₁₀H₁₀ in CH₃CN/CH₂Cl₂, could also be transformed in C₂H₅OH into *nido*-[(PPh₃)₂PtB₁₀H₁₁(OC₂H₅)], so that [(PPh₃)₂PtB₁₀H₁₀] could be the intermediate of the reaction system containing $B_{10}H_{10}^{2-}$ and a platinum halide. However, none of these intermediates or their ultimate products have been structurally characterized. To extend the study of the cage-opening mode and the substituent effect on the cluster geometry, we have carried out the same reaction in methanol and isopropyl alcohol, and report here the structures of the three title platinaboranes, *i.e.* (I), (II) and (III).
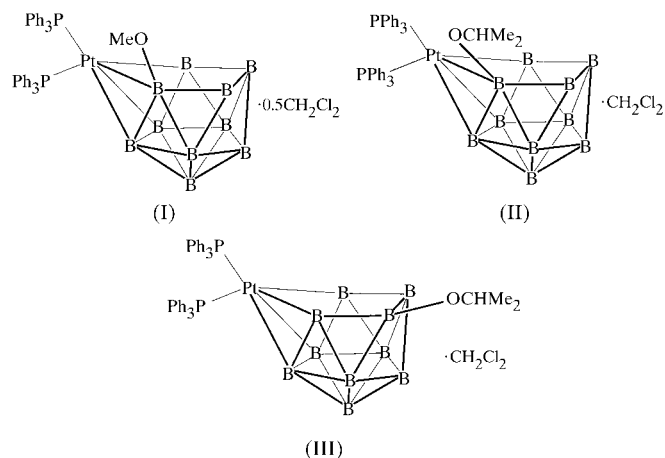


As expected, in compounds (I)–(III), 11-vertex *nido* clusters are produced, the methoxy group is found to be on atom
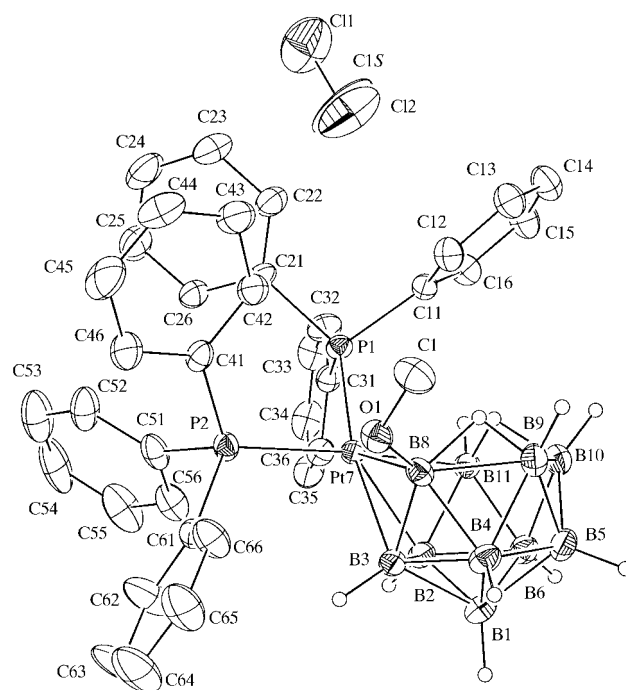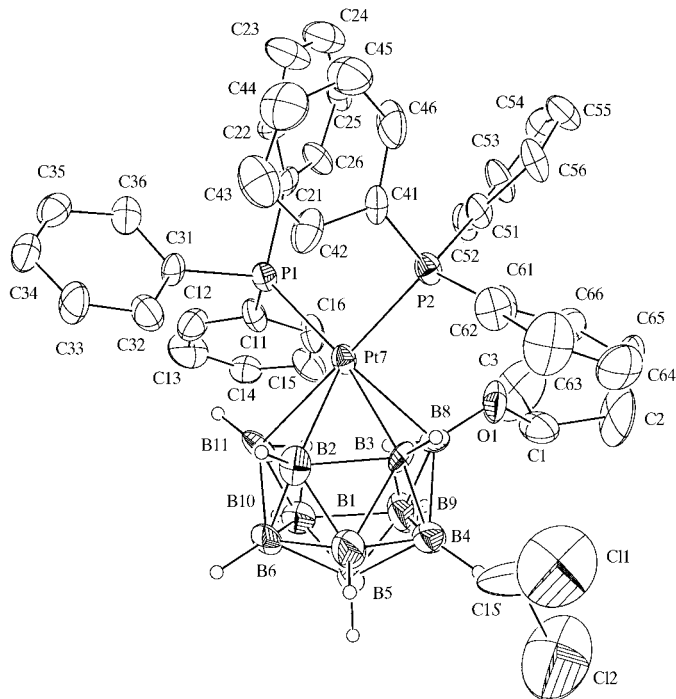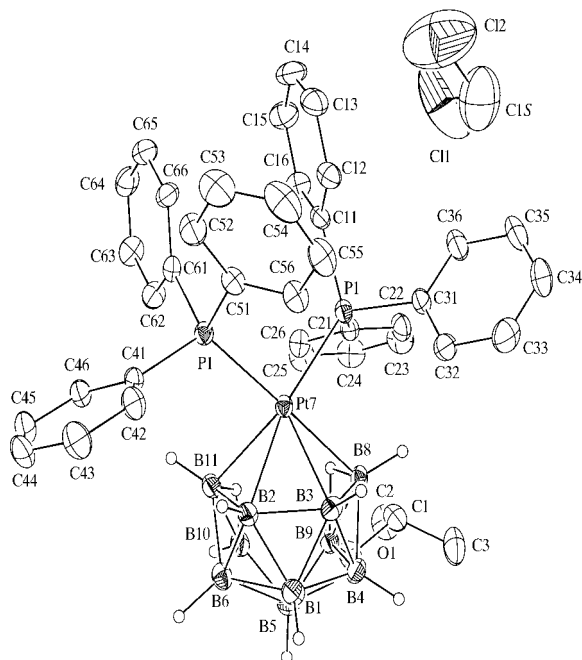


**Figure 1**
The molecular structure of (I) with the atom-numbering scheme and 30% probability displacement ellipsoids. Borane H atoms are shown as small spheres of arbitrary radii and the remainder have been omitted for clarity.

# metal-organic compounds

**Figure 2**
The molecular structure of (II) with the atom-numbering scheme and 30% probability displacement ellipsoids. Borane H atoms are shown as small spheres of arbitrary radii and the remainder have been omitted for clarity.

B8 in (I), and the isopropoxy groups are on atom B8 in (II) and atom B9 in (III). The intramolecular distances and angles, and even the orientations of the PPh$_3$ ligands, are essentially the same in (I)–(III). The Pt—B distances vary in the range



**Figure 3**
The molecular structure of (III) with the atom-numbering scheme and 30% probability displacement ellipsoids. Borane H atoms are shown as small spheres of arbitrary radii and the remainder have been omitted for clarity.

2.214 (7)–2.303 (7) Å in (I), 2.178 (16)–2.326 (16) Å in (II) and 2.205 (6)–2.327 (6) Å in (III); these ranges are similar to but slightly longer than those of the unsubstituted cluster [(PMe$_2$Ph)$_2$PtB$_{10}$H$_{12}$] [2.214 (5)–2.301 (6) Å; Boocock *et al.*, 1981], probably as another consequence of the presence of the alkoxy groups. With regard to the B—O bond lengths, the present values are both close to each other and in the range of those reported for cage–B–O*R* groups (1.371–1.409 Å; Kennedy, 1986).

The present three structures, along with the related examples described above, suggest that the reaction of Pt*X*$_2$(P*R*$_3$)$_2$ in alcohols is so complex that alcohols could attack on the (opened) cage intermediates from different positions. It should be noted that a number of the 1,2-bis(diphenylphosphinoethane) and PMe$_2$Ph relatives of the title compounds have been prepared, namely, the mono-substituted 8-O*R* or 9-O*R* compounds (*R* is Me or Et), but these have unfortunately not been structurally characterized (Kennedy, 1986).

## Experimental

The synthesis of compound (I) was carried out by the reaction of [RuCl$_2$(PPh$_3$)$_3$] (0.38 g, 0.4 mmol), [PtCl$_2$(PPh$_3$)$_2$] (0.32 g, 0.4 mmol) and (NEt$_4$)$_2$B$_{10}$H$_{10}$ (0.16 g, 0.4 mmol) in refluxing methanol (65 ml) for 68 h under dry nitrogen. The resulting mixture was filtered. The yellow precipitate was dissolved in a minimum of dichloromethane and chromatographed using dichloromethane/light petroleum (b.p. 303–333 K) (4:1) as the eluting medium to give compound (I) ($R_F$ = 0.72). Compounds (II) and (III) were synthesized by the reaction of [PtCl$_2$(PPh$_3$)$_2$] (0.284 g, 0.35 mmol) and (NEt$_4$)$_2$B$_{10}$H$_{10}$ (0.265 g, 0.7 mmol) with $^i$PrOH under reflux for 132 h under an atmosphere of dry nitrogen. After filtration, the resulting solution was reduced in volume and chromatographed using dichloromethane/light petrolem (4:1) as the eluting medium to give the two compounds at $R_F$ = 0.83 for (II) and $R_F$ = 0.45 for (III). All three products were recrystallized from *n*-hexane–dichloromethane solution.

### Compound (I)

*Crystal data*

| | |
|---|---|
| [Pt(CH$_{14}$B$_{10}$O)(C$_{18}$H$_{15}$P)$_2$]·<br>0.5CH$_2$Cl$_2$ | $D_x$ = 1.426 Mg m$^{-3}$<br>Mo *K*$\alpha$ radiation |
| $M_r$ = 912.32 | Cell parameters from 25 |
| Monoclinic, *P*2$_1$/*n* | reflections |
| *a* = 12.850 (2) Å | $\theta$ = 6.8–10.8° |
| *b* = 25.824 (7) Å | $\mu$ = 3.47 mm$^{-1}$ |
| *c* = 13.308 (2) Å | *T* = 293 (2) K |
| $\beta$ = 105.770 (10)° | Prism, yellow |
| *V* = 4249.9 (15) Å$^3$ | 0.3 × 0.2 × 0.2 mm |
| *Z* = 4 | |

*Data collection*

| | |
|---|---|
| Rigaku AFC-7*R* diffractometer | $R_{int}$ = 0.048 |
| $\theta$/2$\theta$ scans | $\theta_{max}$ = 25° |
| Absorption correction: $\psi$ scan | *h* = 0 → 13 |
| (North *et al.*, 1968) | *k* = 0 → 30 |
| $T_{min}$ = 0.423, $T_{max}$ = 0.544 | *l* = −15 → 15 |
| 7336 measured reflections | 3 standard reflections |
| 6984 independent reflections | every 200 reflections |
| 5607 reflections with *I* > 2$\sigma$(*I*) | intensity decay: −1.3% |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0601P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | $+ 4.5436P]$ |
| $wR(F^2) = 0.105$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{max} = 0.030$ |
| 6984 reflections | $\Delta\rho_{max} = 1.98$ e Å$^{-3}$ |
| 495 parameters | $\Delta\rho_{min} = -1.71$ e Å$^{-3}$ |
| H atoms treated by a mixture of independent and constrained refinement | |

## Compound (II)

### Crystal data

| | |
|---|---|
| [Pt(C$_3$H$_{18}$B$_{10}$O)(C$_{18}$H$_{15}$P)$_2$]·CH$_2$Cl$_2$ | $D_x = 1.472$ Mg m$^{-3}$ |
| $M_r = 982.83$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 25 reflections |
| $a = 11.114$ (3) Å | $\theta = 9–13.2°$ |
| $b = 21.634$ (8) Å | $\mu = 3.39$ mm$^{-1}$ |
| $c = 18.990$ (8) Å | $T = 293$ (2) K |
| $\beta = 103.75$ (3)° | Plate, yellow |
| $V = 4435$ (3) Å$^3$ | $0.42 \times 0.27 \times 0.07$ mm |
| $Z = 4$ | |

### Data collection

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.081$ |
| $\theta/2\theta$ scans | $\theta_{max} = 25.1°$ |
| Absorption correction: $\psi$ scan (North et al., 1968) | $h = -13 \rightarrow 12$ |
| | $k = 0 \rightarrow 25$ |
| $T_{min} = 0.330$, $T_{max} = 0.797$ | $l = 0 \rightarrow 22$ |
| 8141 measured reflections | 3 standard reflections |
| 7894 independent reflections | every 200 reflections |
| 4066 reflections with $I > 2\sigma(I)$ | intensity decay: 5.4% |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.069$ | $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ |
| $wR(F^2) = 0.238$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.38$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 7894 reflections | $\Delta\rho_{max} = 2.19$ e Å$^{-3}$ |
| 507 parameters | $\Delta\rho_{min} = -3.02$ e Å$^{-3}$ |

## Compound (III)

### Crystal data

| | |
|---|---|
| [Pt(C$_3$H$_{18}$B$_{10}$O)(C$_{18}$H$_{15}$P)$_2$]·CH$_2$Cl$_2$ | $D_x = 1.459$ Mg m$^{-3}$ |
| $M_r = 982.83$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 22 reflections |
| $a = 13.435$ (3) Å | $\theta = 9.1–10.8°$ |
| $b = 17.864$ (4) Å | $\mu = 3.36$ mm$^{-1}$ |
| $c = 19.383$ (4) Å | $T = 293$ (2) K |
| $\beta = 105.94$ (2)° | Square prism, red |
| $V = 4473.1$ (17) Å$^3$ | $0.44 \times 0.34 \times 0.32$ mm |
| $Z = 4$ | |

### Data collection

| | |
|---|---|
| Rigaku AFC-7R diffractometer | $R_{int} = 0.048$ |
| $\theta/2\theta$ scans | $\theta_{max} = 25°$ |
| Absorption correction: $\psi$ scan (North et al., 1968) | $h = 0 \rightarrow 15$ |
| | $k = 0 \rightarrow 21$ |
| $T_{min} = 0.320$, $T_{max} = 0.413$ | $l = -23 \rightarrow 22$ |
| 8222 measured reflections | 3 standard reflections |
| 7865 independent reflections | every 200 reflections |
| 6198 reflections with $I > 2\sigma(I)$ | intensity decay: 0.3% |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0575P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | $+ 0.5166P]$ |
| $wR(F^2) = 0.096$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} = 0.002$ |
| 7865 reflections | $\Delta\rho_{max} = 2.30$ e Å$^{-3}$ |
| 549 parameters | $\Delta\rho_{min} = -0.99$ e Å$^{-3}$ |
| H atoms treated by a mixture of independent and constrained refinement | |

H atoms, other than the B—H—B bridging atoms, were treated as riding, with B—H(general), C—H(phenyl), C—H(–CH), C—H(–CH$_2$) and C—H(–CH$_3$) distances of 1.10, 0.93, 0.98, 0.97 and 0.96 Å, respectively. In all three compounds, the bridging H atoms were refined isotropically.

For compounds (I) and (III), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). For compound (II), data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *Manual*; data reduction: *SDP-Plus* (Frenz, 1985). For all three compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1151). Services for accessing these data are described at the back of the journal.

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