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Nickel and Platinum σ-Bonded Derivatives of Corannulene

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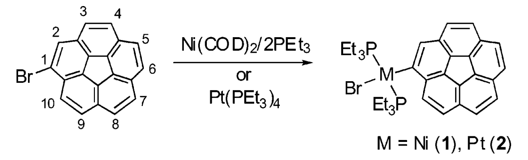
Summary: Organometallic corannulene derivatives with nickel and platinum σ-bonded to the edge have been prepared by oxidative addition of bromocorannulenes to Ni(COD)$_2$/2PEt$_3$ and Pt(PEt$_3$)$_4$.

The discovery of fullerenes[1−3] has stimulated research in polycyclic aromatic hydrocarbons, especially "fullerene fragments" such as corannulene.[4−8] Part of this research has involved organometallic derivatives,[9] and several π-bonded metal complexes of corannulene have been reported.[10−13] Here we report the first σ-bonded metal complexes of corannulene as part of an overall project on σ-bonded metal complexes of polycyclic aromatic carbon compounds.[14]

Ni(COD)$_2$ addition to a mixture of 2 equiv of PEt$_3$ and bromocorannulene[7] results in the immediate formation of a yellow-brown solution, from which yellow-brown *trans*-Ni(PEt$_3$)$_2$(Br)(corannulenyl) (**1**) is isolated (eq 1).



(1)

The analogous platinum complex, yellow *trans*-Pt(PEt$_3$)$_2$(Br)(corannulenyl) (**2**), is readily obtained from the reaction of Pt(PEt$_3$)$_4$ and bromocorannulene (eq 1).

Crystals of **1** and **2** were subjected to X-ray analysis.[15] The crystals are isomorphous and the compounds isostructural. A drawing of **2** is given in Figure 1, and a similar drawing of **1** is provided in the Supporting Information. Both structures show the expected bonding of the metal center to the corannulene edge, with the metal coordination plane approximately orthogonal to the corannulene bowl. This orientation gives inequivalent phosphine ligands with one exo (P1) and one endo (P2) to the bowl.

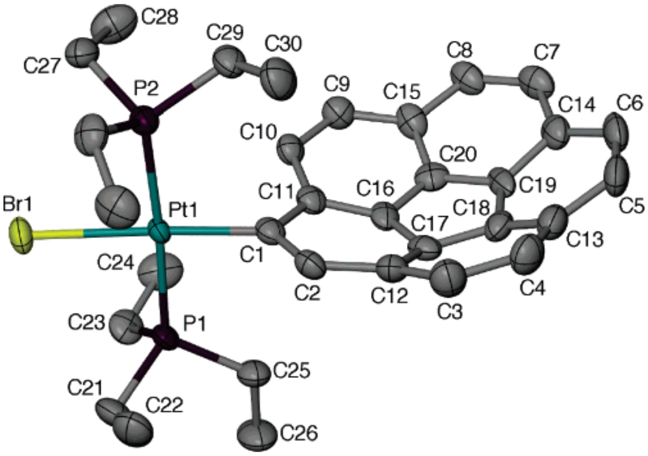


Figure 1. Drawing of *trans*-Pt(PEt$_3$)$_2$(Br)(corannulenyl) (**2**) (50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected distances (Å) and angles (deg) are as follows. **1**: Ni1−Br1 = 2.3551(7), Ni1−C1 = 1.880(4), C1−C2 = 1.429(6), C1−C11 = 1.446(6); C2−C1−C11 = 119.1(4), C2−C1−Ni1 = 120.7(3), C11−C1−Ni1 = 120.2(3). **2**: Pt1−Br1 = 2.5213(4), Pt1−C1 = 2.008(4), C1−C2 = 1.416(5), C1−C11 = 1.458(6); C2−C1−C11 = 118.4(4), C2−C1−Pt1 = 121.9(3), C11−C1−Pt1 = 119.7(3).

Consistent with the solid-state structures, solution ^{31}P NMR spectra for both **1** and **2** show two equal-intensity peaks at −70 °C, with **2** also displaying ^{195}Pt satellites ($J_{\mathrm{PPt}} = 2672$ Hz, $J_{\mathrm{P'Pt}} = 2666$ Hz). Warming the samples causes broadening and coalescence (**1**, $T_c = -28$ °C; **2**, $T_c = -23$ °C) of the two peaks, giving at ambient temperatures a single averaged peak (11.22 and 12.63 ppm, respectively). The $\Delta G^{\ddagger}$ value for the exchange process for **1** is 11.6(1) kcal/mol, and that for **2** is

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(15) X-ray crystallography: Siemens SMART CCD diffractometer (173 K), refinement on F^2 (SHELXL). Compound **1**: C$_{32}$H$_{39}$BrNiP$_2$, a = 12.743(2) Å, b = 15.139(3) Å, c = 15.564(3) Å, β = 105.193(3)°, monoclinic, $P2_1/c$, Z = 4, R1 = 0.0492. Compound **2**: C$_{32}$H$_{39}$BrP$_2$Pt, a = 12.9473(6) Å, b = 15.1634(7) Å, c = 15.5910(8) Å, β = 104.441(1)°, monoclinic, $P2_1/c$, Z = 4, R1 = 0.0278. Compound *trans*-**3**/*trans*-**4**: C$_{32}$H$_{36}$Br$_4$P$_2$Pt, a = 13.7981(18) Å, b = 30.367(4) Å, c = 31.554(4) Å, β = 94.439(3)°, monoclinic, $P2_1/n$, Z = 16, R1 = 0.0843. Compound *trans*-**5**/*trans*-**8**: C$_{44}$H$_{66.37}$Br$_{3.63}$P$_4$Pt$_2$·0.5C$_7$H$_8$, a = 9.6046(4) Å, b = 27.3175(11) Å, c = 20.0055(9) Å, β = 96.583(1)°, monoclinic, $P2_1/c$, Z = 4, R1 = 0.0400.

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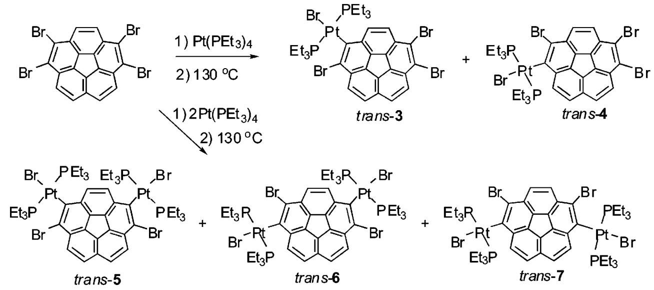
Scheme 1



12.2(1) kcal/mol. The averaging of the endo and exo phosphine ligands may be due either to bowl inversion or rotation about the M−C bond. Given the similarity of the energy barriers for the process to the known bowl inversion barriers for simple corannulenes[16,17] (10−11 kcal/mol), we tentatively attribute the averaging to bowl inversion.

^{1}H NMR spectra for **1** and **2** in the aromatic region are similar to those of bromocorannulene,[7,18] but with downfield shifts of the 2- and 10-protons (see eq 1 or Figure 1 for numbering) and the presence of ^{195}Pt satellites for the 2-proton in **2**. Similarly, the ^{13}C NMR spectra show downfield shifts of the 1-carbons and coupling to the ^{31}P centers.

In a similar reaction, a toluene solution of 1,2,5,6-tetrabromocorannulene[8,19] was treated with 1 equiv of $Pt(PEt_3)_4$ at 25 °C. ^{31}P NMR spectroscopy of the reaction mixture suggests the formation of the cis oxidative addition products *cis*-$Pt(PEt_3)_2(Br)$(1,5,6-tribromocorannulen-2-yl) (*cis*-**3**) and *cis*-$Pt(PEt_3)_2(Br)$(2,5,6-tribromocorannulen-1-yl) (*cis*-**4**) in a 1:1 ratio. However, these compounds were not further characterized, and the reaction mixture was heated at 130 °C to give a mixture of *trans*-$Pt(PEt_3)_2(Br)$(1,5,6-tribromocorannulen-2-yl) (*trans*-**3**) and *trans*-$Pt(PEt_3)_2(Br)$(2,5,6-tribromocorannulen-1-yl) (*trans*-**4**) (Scheme 1). The ^{31}P NMR spectrum of the mixture shows two singlets with satellites in a ratio of ca. 2:3, downfield from those for **2**. The mixture can be separated by column chromatography, allowing the isolation of pure *trans*-**3** (first to elute) and *trans*-**4**. *trans*-**4** is identified as the major product. Crystals suitable for X-ray analysis[15] were obtained from the concentrated reaction mixture and consist of a cocrystallized disordered mixture of *trans*-**3** and *trans*-**4** (see the Supporting Information). Although the disorder and large crystal axes adversely affected the structural results, a *trans*-**3** to *trans*-**4** ratio of ∼1:2 was clearly obtained. A ^{31}P NMR spectrum of the dissolved crystals confirmed the 1:2 ratio, and the NMR spectroscopic assignments of the two isomers.

Increasing the amount of PtL_4 to 2 equiv in the reaction with 1,2,5,6-tetrabromocorannulene probably initially gives cis addition products, but these were immediately converted to the trans products by heating (Scheme 1). A ^{31}P NMR spectrum of the resulting reaction mixture shows three overlapping unequal peaks assigned to *trans*-$\{Pt(PEt_3)_2(Br)\}_2$(1,6-dibromocorannulene-2,5-diyl) (*trans*-**5**), *trans*-$\{Pt(PEt_3)_2(Br)\}_2$-(2,6-dibromocorannulene-1,5-diyl) (*trans*-**6**), and *trans*-$\{Pt(PEt_3)_2(Br)\}_2$(2,5-dibromocorannulene-1,6-diyl) (trans-**7**). Careful column chromatography allows separation of the isomers, with *trans*-**6** eluting first and *trans*-**7** last. Crystals obtained from the reaction mixture were subjected to X-ray analysis[15] and were found to be those of *trans*-**5** (Figure 2). However, the bromine atom at the 1-position displayed an unusually large thermal parameter. Occupancy refinement indicated the presence of Br in only ∼63% of the molecules. NMR spectra of the dissolved crystals show *trans*-**5** but also peaks consistent with *trans*-$\{Pt(PEt_3)_2(Br)\}_2$(1-bromocorannulene-2,5-diyl) (*trans*-**8**), the 1-debrominated analogue of *trans*-**5**. Integration gives a *trans*-**5**:*trans*-**8** ratio of 60:40, consistent with the X-ray results. Reexamination of the NMR data for the reaction mixture shows only very small amounts of *trans*-**8** and other small peaks that may be attributed to additional debromination isomers. Competing dehalogenation in oxidative addition reactions of aryl halides has been reported.[20]

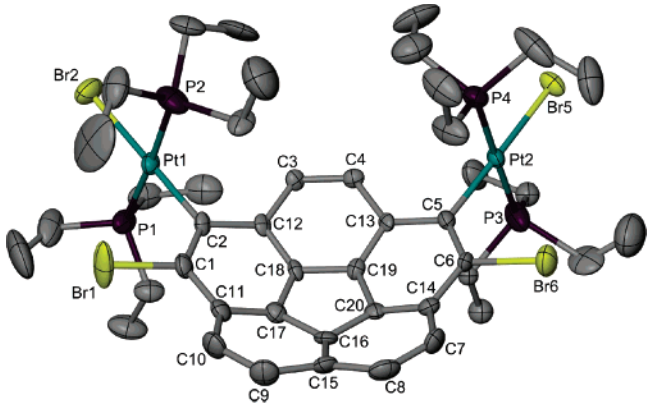


Figure 2. Drawing of *trans*-$Pt_2(PEt_3)_4(Br)_2$(1,6-dibromocorannulene-2,5-diyl), (*trans*-**5**)/*trans*-$Pt_2(PEt_3)_4(Br)_2$(1-bromocorannulene-2,5-diyl) (*trans*-**8**) (50% probability ellipsoids, Br1 at 63% occupancy, hydrogen atoms omitted for clarity). Only one orientation of the disordered Et groups on P2 and P3 is shown. Selected distances (Å) and angles (deg): Pt1−C2 = 2.011(7), Pt2−C5 = 2.019(6), C1−C2 = 1.397(9), C2−C12 = 1.461(9), C5−C6 = 1.397(9), C5−C13 = 1.468(9); C1−C2−C12 = 117.2(6), C1−C2−Pt1 = 122.1(5), C12−C2−Pt1 = 120.6(5), C6−C5−C13 = 117.0(6), C6−C5−Pt2 = 124.0(5), C13−C5−Pt2 = 119.0(5).

In conclusion, oxidative addition reactions of brominated corannulenes with Ni(0) and Pt(0) complexes have yielded the first σ-bonded metal complexes of corannulene. With 1,2,5,6-tetrabromocorannulene selective single and double oxidative addition reactions are possible, giving monoplatinum or diplatinum complexes. Future effort will be devoted to oxidative addition reactions of more highly halogenated corannulenes and reduction of the oxidative addition products.[14]

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Supporting Information Available: Text, figures, and tables giving synthetic procedures and characterization data for **1**−**8**; crystal data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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