

A weakly coordinating anion as a tripodal “Br₃”-ligand for platinum(IV) — Structure of [(*closo*-CB₁₁H₆Br₆)PtMe₃]¹

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Abstract: Synthesis, structure, and NMR spectroscopic data for [(*closo*-CB₁₁H₆Br₆)PtMe₃] are reported. This neutral platinum(IV) complex contains the *closo*-CB₁₁H₆Br₆[−] anion bonded to the trimethylplatinum(IV) cation via three boron-bound bromines. *closo*-CB₁₁H₆Br₆[−], which often acts as weakly coordinating or even non-coordinating anion, adopts here a role still very rare for this anion: it acts as a tripodal capping ligand enabling a pseudo-octahedral geometry at a d⁶ metal center. Three bromines from the lower hemisphere of the hexahalogenated carboranate coordinate to Pt(IV), and distortions from ideal octahedral angles at Pt are marginal (<3°). Pt-Br bond lengths are 2.7279(18), 2.7129(17), and 2.7671(18) Å. Using the ²J_{PtH} coupling constant of Pt-bonded methyl groups (79.0 Hz) as indicator of the donor strength of the tripodal cap, the prediction is obtained that *closo*-CB₁₁H₆Br₆[−] is a relatively weak donor toward the trimethylplatinum(IV) cation. Ligand competition equilibria can be expected to depend on both the intrinsic donor strengths of competing ligands and on the effects of charge and geometry. We observe that *closo*-CB₁₁H₆Br₆[−] is capable of replacing acetone from Me₃Pt(acetone)₃⁺, whereas BF₄[−] counterion is unable to replace acetone under similar conditions.

Key words: non-coordinating anion, platinum(IV), trimethyl, *closo*-carboranate, tripodal, trans-influence, NMR spectroscopy.

Résumé : On a réalisé la synthèse et on a déterminé la structure et les données de spectroscopie RMN relative au [(*closo*-CB₁₁H₆Br₆)PtMe₃]. Ce complexe neutre de platine(IV) contient un anion *closo*-CB₁₁H₆Br₆[−] lié à un cation triméthylplatine(IV) par le biais de trois atomes de bore liés à des atomes de brome. L'anion *closo*-CB₁₁H₆Br₆[−] qui agit souvent comme un anion de coordination faible, qui est même quelquefois non coordonnant, adopte dans notre cas un rôle encore plus rare pour cet anion, à savoir celui de ligand tripode qui sert de cap et qui permet d'avoir une géométrie pseudo-tétraédrique au niveau d⁶ du centre métallique. Les trois atomes de brome de la partie inférieure de l'hémisphère du carboranate hexahalogéné se lient par coordination au Pt(IV) et les distorsions par rapport aux angles octaédriques idéaux au niveau du platine sont marginales (<3°), alors que les longueurs des liaisons Pt-Br sont de 2,7279(18), 2,7129(17) et 2,6771(18) Å. Utilisant la constante de couplage ²J_{PtH} des groupes méthyles liés au platine (79,0 Hz) comme indicateur de la force du cap trigonal, on arrive à la prédiction que l'anion *closo*-CB₁₁H₆Br₆[−] est un donneur relativement faible par rapport au cation triméthylplatine(IV). On peut s'attendre à ce que l'équilibre de compétition pour le ligand dépende à la fois des forces intrinsèques comme donneurs des ligands en compétition et sur les effets de charge et de géométrie. On a observé que l'anion *closo*-CB₁₁H₆Br₆[−] est capable de remplacer l'acétone du complexe Me₃Pt(acétone)₃⁺ alors que le contre-ion BF₄[−] n'est pas capable de remplacer l'acétone dans de telles conditions.

Mots-clés : anion non coordonnant, platine(IV), triméthyle, *closo*-carboranate, tripode, influence *trans*, spectroscopie RMN.

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Introduction

The development of noncoordinating (or very weakly coordinating) anions has led to tremendous progress in the

field of highly Brønsted-acidic or Lewis-acidic species (1). *Closo*-carboranates (2) have proven excellent alternatives to tetraarylborates. Furthermore, the *closo*-carboranate framework seems to be nontoxic (3). Carboranates have recently

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been used, for example, as counter-anions for the isolation of reactive silylium ions (4), as well as to furnish inert conjugate bases for superacids used to obtain crystalline hydronium ions and protonated arenes (5). Cluster anions such as *closo*-CB₁₁H₁₂⁻ and substituted derivatives often act as noncoordinating or very weakly coordinating anions in systems containing transition metals (2, 6, 7). Cases do exist, however, where *closo*-carboranates coordinate to metal centers. Even for the rather electron-deficient carboranate *closo*-CB₁₁H₆Br₆⁻, examples have been reported recently where coordination to metals occurs, and it is just beginning to become clear to which metals this carboranate may bind and under which conditions. The ability of *closo*-CB₁₁H₆Br₆⁻ to coordinate should depend on the metal in question, its oxidation state, and its ligand environment. The vast majority of examples where metal coordination to *closo*-CB₁₁H₆Br₆⁻ and closely related carboranates occurs involve the highly Lewis-acidic Ag(I) (8, 9). A few d⁸ metal examples are known where coordination to rhodium(I) (7a) or iridium(I) (7a) could be observed. However, only very recently (2007) a crystallographically characterized example was reported where CB₁₁H₆Br₆⁻ acted as a tripodal ligand toward a d⁶ metal center, namely toward a rhodium(III) dihydride supported by an additional tricyclohexylphosphine (10). The question arises as to whether the ability of *closo*-CB₁₁H₆Br₆⁻ to act as a tripodal cap for an octahedral complex may be extended to other platinum group metals. An excellent candidate is the trimethylplatinum(IV) unit, an often very stable moiety. A recent determination of the Lewis-acidity of the Me₃Pt⁺ unit found it to be moderately Lewis-acidic (11). We can now report here that a stable pseudo-octahedral complex is formed when *closo*-CB₁₁H₆Br₆⁻ reacts with a good source of the Me₃Pt⁺ synthon.

Results and discussion

Synthesis

A salt metathesis of the cesium carboranate (12) [Cs][*closo*-CB₁₁H₆Br₆] with tetrameric trimethylplatinum(IV) triflate (13), a good source of the Me₃Pt⁺ synthon, in a weakly coordinating nonpolar solvent (such as benzene) forms the highly soluble [(*closo*-CB₁₁H₆Br₆)PtMe₃] in quantitative yield, while insoluble cesium triflate (CsOTf = Cs(F₃CSO₃)) precipitates. In dry form, the compound is isolated as a shiny white microcrystalline powder. While we avoided exposing the compound to significant amounts of water, we found it very stable towards air or oxygen. We found no decomposition in noncoordinating solvents at room temperature and very little decomposition on a sample that was heated to 60 °C in CD₂Cl₂ for 8 months! Considering that many trimethylplatinum(IV) complexes undergo carbon-carbon reductive elimination (to form ethane) rather readily, the inertness of [(*closo*-CB₁₁H₆Br₆)PtMe₃] towards reductive elimination may appear surprising at first but is entirely in agreement with our current very detailed knowledge

of reductive elimination in platinum(IV) systems: sp³-sp³ carbon-carbon reductive elimination from platinum(IV) is always *relatively* slow, for example, much slower than carbon-hydrogen reductive elimination in comparable methyl(hydrido) systems (14). Two factors have major influence on the barrier to C-C reductive elimination: (i) the ease of formation of a five-coordinate intermediate (15) and (ii) electronic effects, namely the donor strength of the spectator ligands. Alkyl-alkyl reductive elimination from Pt(IV) generally requires that the complex can assume a five-coordinate geometry (14-18), and the barrier to forming such a five-coordinate geometry contributes to the overall barrier for reductive elimination. While the ground-state geometry of [(*closo*-CB₁₁H₆Br₆)PtMe₃] is six-coordinate and octahedral (see below), a five-coordinate geometry should be accessible (if the tripodal carboranate partially dechelates) and only slightly uphill. Electronic effects are most likely responsible for the inertness observed here: for C-C reductive elimination to be fast, the coordination environment has to contain strongly donating spectator ligands (such as phosphines (14, 16, 17) systems having a less donating nitrogen-based ligand environment are comparably resistant to reductive elimination) (17), and the observed lack of reductive elimination for [(*closo*-CB₁₁H₆Br₆)PtMe₃] indicates that *closo*-CB₁₁H₆Br₆⁻ acts as a rather weakly donating spectator ligand.

X-ray crystal structure

Crystals suitable for X-ray diffraction were obtained by slowly reducing the volume of a saturated dichloromethane solution of [(*closo*-CB₁₁H₆Br₆)PtMe₃] under nitrogen. Data were collected on a Nonius-Kappa CCD diffractometer at 150(1) K, and the crystal structure was solved by direct methods and refined on *F*² against all reflections.³ Crystal data are summarized in Table 1. The structure contains discrete units of molecular [(*closo*-CB₁₁H₆Br₆)PtMe₃], shown in Fig. 1 (selected distances and angles in the legend). The most striking feature is the almost perfectly pseudo-octahedral environment of platinum(IV), where deviations from ideal angles are less than 3°. The average of the three Pt-Br distances (2.7279(18), 2.7129(17), 2.7671(18) Å) is 2.74 Å. This is 8% longer than the Pt-Br distance for Br⁻ ion coordinated to platinum(IV) in a terminal fashion (2.5394(6) Å for Pt-Br in a bromotriorganylplatinum(IV) complex chelated by a substituted bipyridine (19)) but only 3% longer than the Pt-Br distance in tetrameric trimethylplatinum(IV) bromide (20), which contains triply bridging bromide (2.67(1) Å).

Coupling constant correlation

The trimethylplatinum(IV) unit is a convenient tool to gauge the donor strength of coordinated ligands (21). *Trans*-influence effects weaken a Pt-CH₃ bond proportionally to the donor strength of the ligand *trans* to it, an effect that transmits into the ²J_{PtH} coupling constant of the methyl.

³Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3775. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 676243 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via 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 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystal and structure refinement for [(*closo*-CB₁₁H₆Br₆)PtMe₃].

Empirical formula	C ₄ H ₁₅ B ₁₁ Br ₆ Pt
Formula weight	856.62
Temperature (K)	150(2)
Wavelength (Å)	0.710 73
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.3965(9)
<i>b</i> (Å)	11.8815(4)
<i>c</i> (Å)	14.8355(10)
α (°)	90
β (°)	90.16
γ (°)	90
<i>V</i> (Å ³)	2008.8(2)
<i>Z</i>	4
<i>D</i> _{calcd} (Mg/m ³)	2.832
Absorption coefficient (mm ⁻¹)	18.902
<i>F</i> (000)	1528
Crystal size	0.10 mm × 0.08 mm × 0.06 mm
Theta range for data collection	2.75°–25.00°
Index ranges	–13 ≤ <i>h</i> ≤ 13, –14 ≤ <i>k</i> ≤ 14, –12 ≤ <i>l</i> ≤ 17
Reflections collected	3491
Independent reflections	3491 [<i>R</i> (int) = 0.145]
Completeness to theta = 25.00°	98.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.359 and 0.139
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data, restraints, parameters	3491, 0, 213
Goodness-of-fit on <i>F</i> ²	1.033
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0581, <i>wR</i> ₂ = 0.1344
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0746, <i>wR</i> ₂ = 0.1445
Largest diff. peak and hole (e, Å ⁻³)	2.751, –3.516

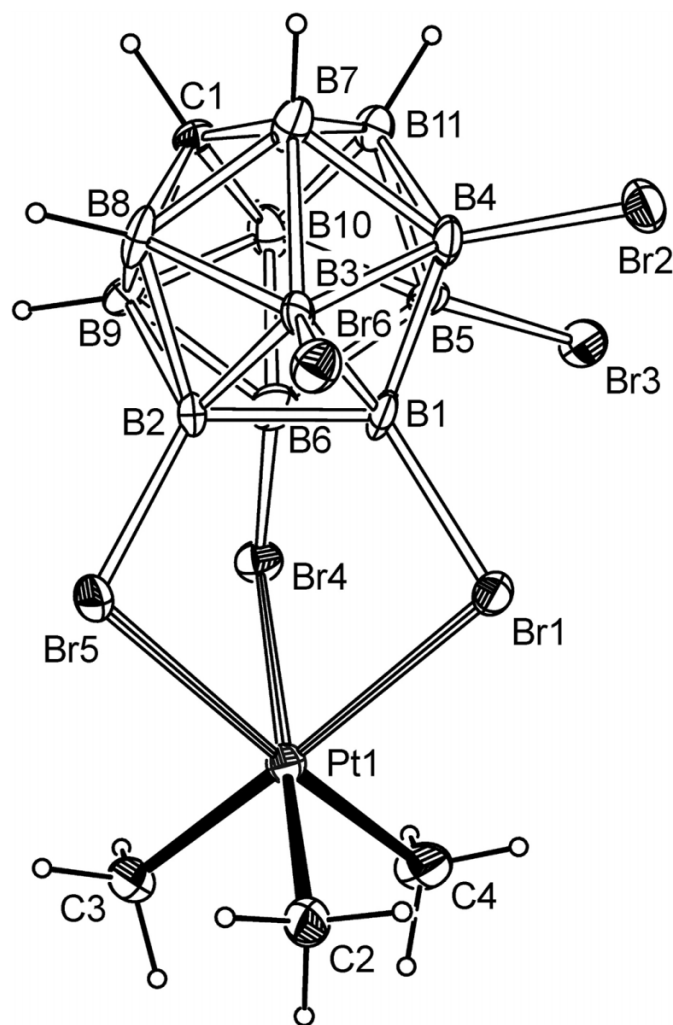
Capping the three positions *trans* to the *fac*-trimethyls in a trimethylplatinum(IV) complex with three strongly donating phosphine donors leads to a very low coupling constant, and ²*J*_{PtH} = 55 Hz is observed for the complex containing the tris(phosphino)borate PhB(CH₂PPh₂)₃[–] (22). Having three relatively donating nitrogen donors normally leads to a ²*J*_{PtH} around 72 Hz. The ²*J*_{PtH} coupling constant is sensitive to fairly subtle electronic effects related to the donor strength of the ligand. For example, ²*J*_{PtH} = 72 Hz is observed in the presence of the tris(pyrazolyl)methane cap *trans* to PtMe₃ (23), whereas ²*J*_{PtH} = 70 Hz is observed in the presence of the more electron-rich tris(3,5-dimethylpyrazolyl)borate cap *trans* to PtMe₃ (21c). An analogous complex having trifluoromethyl groups instead of methyl groups on the pyrazolates is less donating because of inductive effects, and an increased ²*J*_{PtH} is observed for the Pt methyls, namely 75.4 Hz (21c). Among the weakest donors toward platinum(IV) are oxygen donors, and a weakly coordinating “O₃” environment typically leads to a ²*J*_{PtH} value for platinum trimethyls between 76 and 82 Hz (21c). The 82 Hz extreme value belongs to trimethylplatinum(IV) in the tetrameric structure {Me₃Pt(OTf)}₄, which contains octahedral platinum(IV) and triply bridging triflate (13, 24). The ²*J*_{PtH} value for the methyls in the aqua complex Me₃Pt(OH₂)₃⁺ is 80.6 Hz (25). The coupling constant observed for [(*closo*-CB₁₁H₆Br₆)PtMe₃], 79.0 Hz (in benzene-*d*₆), leads us to

conclude that the “Br₃” environment is roughly as donating toward Pt(IV) as an oxygen-donor environment. It will be of interest to investigate how efficiently *closo*-CB₁₁H₆Br₆[–] competes for the Me₃Pt⁺ unit if other relatively weakly donating ligands are present in an equilibrium mixture.

Ligand competition experiments

We feel that the ²*J*_{PtH} of the platinum-bound methyls is a reasonable indicator of the ligand donor strength because of *trans*-influence arguments, as discussed above. Regarding the strengths of the ligand-metal interactions in a thermodynamic sense, as measured in complexation equilibria, we would expect that a semi-quantitative prediction should be possible based on donor strength judged by ²*J*_{PtH}. An absolutely accurate prediction cannot be expected, in particular in cases where ²*J*_{PtH} values are very similar and in cases where a competition between ligands bearing different charges or having very different steric requirements is considered. To test our hypothesis that donor strengths as indicated by ²*J*_{PtH} have significant value for predicting complexation equilibria, we performed several experiments where *closo*-CB₁₁H₆Br₆[–] was competing against other ligands for complexation to Me₃Pt⁺. We reacted [(*closo*-CB₁₁H₆Br₆)PtMe₃], which contains a tripodal monoanionic ligand, with the tripodal monoanionic ligand CpCo[P(O)(OCH₃)₂]₃[–] (“Kläui ligand”, added as the sodium

Fig. 1. Molecular structure of $[(\text{closo-CB}_{11}\text{H}_6\text{Br}_6)\text{PtMe}_3]$, using 30% probability thermal ellipsoids. Selected distances (Å) and angles ($^\circ$): Pt1–C2 2.006(17); Pt1–C3 2.047(18); Pt1–C4 2.036(18); Pt1–Br1 2.7279(18); Pt1–Br4 2.7129(17); Pt1–Br5 2.7671(18); Br1–B1 1.961(15); Br2–B4 1.968(19); Br3–B5 1.979(19); C2–Pt1–C4 89.1(7); C2–Pt1–C3 88.1(7); C4–Pt1–C3 88.3(8); C2–Pt1–Br4 178.2(6); C4–Pt1–Br4 92.3(5); C3–Pt1–Br4 92.9(5); C2–Pt1–Br1 92.8(5); C4–Pt1–Br1 94.0(6); C3–Pt1–Br1 177.6(5).



salt; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). Based on ${}^2J_{\text{PtH}}$ arguments, it would be expected that the Kläui ligand is more donating (${}^2J_{\text{PtH}} = 78.5$ Hz *trans* to Kläui ligand; ${}^2J_{\text{PtH}} = 79.3$ Hz *trans* to $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ in 1,2-dichloroethane- d_4). In agreement with this prediction, we observed that addition of 1 equiv. of Kläui ligand led to complete decooordination of $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ and to formation of $\{\text{CpCo}[\text{P}(\text{O})(\text{OCH}_3)_2]_3\text{PtMe}_3\}$, as observed by ${}^1\text{H}$ and ${}^{11}\text{B}$ NMR spectra (26). On the other hand, it would be interesting to test for competition equilibria between $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ and ligands where ${}^2J_{\text{PtH}}$ predicts lower donor strength than $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$. We are not aware of any ligand that complies with the above ${}^2J_{\text{PtH}}$ requirement and is tripodal and monoanionic. We therefore decided to use neutral monodentate ligands to test for their ability to coordinate to Pt(IV) and release $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$

as a noncoordinating anion. ${}^2J_{\text{PtH}}$ arguments would predict that acetone is less donating than $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ (${}^2J_{\text{PtH}} = 79.8$ Hz *trans* to acetone, in $\text{Me}_3\text{Pt}(\text{acetone})_3^+$; ${}^2J_{\text{PtH}} = 79.3$ Hz *trans* to $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$; 1,2-dichloroethane- d_4 solvent). Although acetone is charge-neutral, such that there does exist some electrostatic bias towards carboranate-coordination, it still can be expected that a neutral molecule should replace the carboranate if that neutral molecule were vastly more donating than the carboranate. Even after addition of 38 equiv. of acetone to a solution containing $[(\text{closo-CB}_{11}\text{H}_6\text{Br}_6)\text{PtMe}_3]$ (3.5 mmol/L in 1,2-dichloroethane- d_4), we observe no carboranate decooordination (${}^{11}\text{B}$ NMR) and no acetone coordination to Pt (${}^1\text{H}$ NMR). To test for whether a more donating solvent, as judged by ${}^2J_{\text{PtH}}$, leads to carboranate replacement, we used tetrahydrofuran (thf), which we would predict to be more coordinating than $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ (${}^2J_{\text{PtH}} = 76.8$ Hz in $\text{Me}_3\text{Pt}(\text{thf})_3^+$ compared with 79.3 Hz for $[(\text{closo-CB}_{11}\text{H}_6\text{Br}_6)\text{PtMe}_3]$ in 1,2-dichloroethane- d_4). In accord with this prediction, we observed rapid decooordination of $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ when titrating in small amounts of thf to the platinum complex (3.6 mmol/L in 1,2-dichloroethane- d_4), and after the addition of 38 equiv. of thf, the carboranate was essentially fully decoordinated (96%; after addition of 48 equiv. of thf, 100% decooordination was achieved). It seems, indeed, that donor strengths, as judged by ${}^2J_{\text{PtH}}$, have bearing on competition equilibria. Regarding acetone versus a weakly coordinating anion, again it is significant that $\text{Me}_3\text{Pt}(\text{acetone})_3^+$ can be obtained reliably using a BF_4^- counter-ion and even crystallized (29). In contrast, $\text{Me}_3\text{Pt}(\text{acetone})_3^+$ cannot be obtained using $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ anion. We confirmed this by reacting $[\text{Me}_3\text{Pt}(\text{acetone})_3][\text{BF}_4]$ with 0.87 equiv. of $[\text{Cs}][\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$, where we observed partial acetone substitution and carboranate coordination. It should be interesting to compare the coordinating ability of $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ with the coordinating ability of triflate. Both anions are generally regarded as weakly coordinating, and it is known for both anions that they can coordinate to the trimethylplatinum(IV) unit; triflate-coordination to trimethylplatinum(IV) is well-known (13, 24), and $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ coordination to trimethylplatinum(IV) has been shown in the present work. While ${}^2J_{\text{PtH}}$ for Pt–Me is 82.0 Hz in tetrameric trimethyl platinum triflate, $\{\text{Me}_3\text{Pt}(\text{O}_3\text{SCF}_3)_4\}_4$, ${}^2J_{\text{PtH}}$ of 79.0 Hz is observed for $[(\text{closo-CB}_{11}\text{H}_6\text{Br}_6)\text{PtMe}_3]$ (both in CD_2Cl_2), which would indicate that the carboranate is more donating. When we reacted $[(\text{closo-CB}_{11}\text{H}_6\text{Br}_6)\text{PtMe}_3]$ with 0.97 equiv. of a soluble triflate salt, $(\text{NBu}_4)(\text{F}_3\text{CSO}_3)$, in 340 μL of 1,2-dichloroethane- d_4 , we observed partial decooordination (57%) of the $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ anion in the equilibrium mixture, and both the carboranate and triflate were effectively competing for the trimethylplatinum(IV) moiety. Qualitatively, we conclude that triflate and $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ are of very similar coordinating ability toward trimethylplatinum(IV); if triflate were much more donating, 97% of the carboranate would have been released as free noncoordinating anion, as opposed to the 57% free carboranate observed. We remain with a qualitative conclusion regarding the triflate versus $\text{closo-CB}_{11}\text{H}_6\text{Br}_6^-$ competition, since the tetrameric nature of trimethylplatinum triflate leads to a rather complex reaction stoichiometry instead of a straightforward ligand-for-ligand substitution. The reaction

stoichiometry is as follows: $4 [(closo-CB_{11}H_6Br_6)PtMe_3] + 4 NBu_4^+ + 4 F_3CSO_3^- \rightarrow \{Me_3Pt(O_3SCF_3)\}_4 + 4 NBu_4^+ + 4 CB_{11}H_6Br_6^-$. For practical purposes, the coordinating ability of *closo*- $CB_{11}H_6Br_6^-$ toward Me_3Pt^+ may be described as “less coordinating than the Kläui ligand, approximately as coordinating as triflate, more coordinating than tetrafluoroborate”. It should be noted here that this *relatively* high propensity of *closo*- $CB_{11}H_6Br_6^-$ to coordinate to Me_3Pt^+ is likely due to the fact that the bromine donors, “soft” donor atoms, are relatively good ligands for a soft metal such as platinum. Geometric reasons certainly contribute as well, since the Br_3 donor “cap” enables an octahedral geometry for platinum(IV).

Summary and conclusion

The brominated carboranate *closo*- $CB_{11}H_6Br_6^-$ acts as a tripodal Br_3 donor ligand cap in the new compound $[(closo-CB_{11}H_6Br_6)PtMe_3]$, made using a salt metathesis of the cesium carboranate $[Cs][closo-CB_{11}H_6Br_6]$ with tetrameric trimethylplatinum(IV) triflate in nonpolar solvents, where the precipitation of insoluble cesium triflate provides the driving force. The Br_3 donor cap enables an octahedral geometry for platinum(IV). *Closo*- $CB_{11}H_6Br_6^-$ is among the weakly donating ligands towards $PtMe_3^+$ but in effect more coordinating, in this particular system than tetrafluoroborate, since it substitutes acetone from $Me_3Pt(acetone)_3^+$. In contrast, the BF_4^- counter-ion is unable to replace acetone under similar conditions. A reasonable estimate of the donor strengths of ligands for trimethylplatinum(IV) can be obtained using the $^2J_{PtH}$ coupling constant seen for the Pt-bound methyls, and such an approach appears to have qualitative and (or) semi-quantitative predictive power for ligand competition equilibria.

Experimental section

General information, reagents, and precursors

All manipulations involving organometallic compounds were carried out with the use of vacuum line and dry glove box using oven-dried glassware and J. Young NMR tubes. 1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian Gemini 200 MHz, Bruker Avance III 400 MHz NMR, or Unity Inova Varian 500 MHz spectrometers (Mississauga, platinum complexes) or JEOL 400 MHz NMR spectrometer (Ithaca, cesium carboranates).³ ^{19}F NMR data were recorded on a Bruker Avance III 400 MHz NMR (Mississauga) spectrometer at 376 MHz and referenced to an internal standard, neat trifluoroacetic acid (capillary within the sample tube) set at δ 78.50 ppm. $^{11}B\{^1H\}$ and ^{11}B NMR spectra were taken on a JEOL 400 MHz NMR (Ithaca) and Bruker Avance III 400 MHz NMR (Mississauga) spectrometer and referenced relative to neat $BF_3 \cdot OEt_2$ (capillary within the sample tube) set at δ 0 ppm. All NMR spectra were taken at 20 °C unless otherwise noted. Solvent peaks were used as reference: 1H (δ , ppm, dichloromethane- d_2 , 5.32; 1,2-dichloroethane- d_4 , 3.72; benzene- d_6 , 7.16; acetone- d_6 , 2.05), ^{13}C (δ , ppm, dichloromethane- d_2 , 53.8; benzene- d_6 , 128.0; acetone- d_6 , 29.8 (- CD_3)). CD_2Cl_2 (obtained from Cambridge Isotopes, 99.9% D), $ClCD_2CD_2Cl$ and CH_2Cl_2 were dried over CaH_2 and vacuum-transferred before use. $(CD_3)_2CO$

(99.9% D) and $(CH_3)_2CO$ was dried over activated 3 Å molecular sieves. C_6D_6 (99.5% D) and $(CD_3)_2CO$ were purchased from Cambridge Isotopes. Trifluoroacetic acid, 1,2-dichloroethane- d_4 , (99% D), fluorene (98%) were purchased from Sigma-Aldrich. Iodotrimethylplatinum (99.8%) was purchased from Strem Chemicals. Decaborane, used for the synthesis (27) of $CsCB_{11}H_{12}$, precursor for $[Cs][closo-CB_{11}H_6Br_6]$, was purchased from Katchem spol. s.r.o. (Ltd.), Czech Republic. Silver trifluoromethanesulfonate, silver tetrafluoroborate (98%), and tetrabutylammonium trifluoromethanesulfonate ($\geq 99.0\%$) and all other chemicals where a supplier is not explicitly mentioned were purchased from Sigma-Aldrich ($\geq 99.8\%$). Tetrahydrofuran (THF) and benzene (protio and deuterated) were dried over sodium-benzophenone and vacuum-transferred before use. Elemental analyses were conducted at Analytical Laboratory for Environmental Science and Research Training (ANALEST), Toronto, ON, Canada. $Cs[closo-CB_{11}H_6Br_6]$ was synthesized using the literature method (12) from $CsCB_{11}H_{12}$ (27). It was obtained in 75% yield and found to be analytically pure by elemental analysis (Calcd. for $[Cs][closo-CH_6B_{11}Br_6]$: C 1.60, H 0.81; found: C 1.90, H 1.07) and NMR (1H NMR (500 MHz, $(CD_3)_2CO$) δ : 3.07–1.82 (6H, br, B-H); $^{13}C\{^1H\}$ NMR (125 MHz, $(CD_3)_2CO$) δ : 41.71 (C_{cage}); $^{11}B\{^1H\}$ NMR (128.34 MHz, $(CD_3)_2CO$, 22 °C) δ : -2.0 (s, 1B, Br-B opposite to carbon apex), -9.8 (s, 5B, Br-B of lower ring), -20.3 (s, 5B, H-B)). The tetrameric trimethylplatinum(IV) triflate precursor was synthesized using literature methods in THF solvent (13). $\{Me_3Pt(OTf)\}_4$: 1H NMR 500 MHz, (C_6D_6) δ : 1.49 (9H, s+d, Pt-Me₃, $^2J_{PtH}$ = 82.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ : -9.71 (s+d, Pt-Me₃, J_{PtC} = 827.5 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ : -79.10 (s, 3F).

$[(closo-CB_{11}H_6Br_6)PtMe_3]$

$[Cs][closo-CB_{11}H_6Br_6]$ (11.4 mg, 749.3 g/mol, 0.0153 mmol) was added to a 540 μ L of benzene- d_6 solution containing $\{Me_3Pt(OTf)\}_4$ (6.0 mg, 0.0154 mmol in Pt) and shaken for 30 s. Sonication of the solution aids in the dissolution of $CsCB_{11}H_6Br_6$. The reaction was monitored by 1H NMR spectroscopy using the platinum methyl signal and was completed within 1 h. The solvent was removed under vacuum and extracted with dichloromethane (where $CsOTf$ is insoluble). The residue was washed with 1 mL portions of dichloromethane, allowing $CsOTf$ to settle between each washing. Removal of the solvent yielded the product as white crystals. NMR conversion is quantitative, isolated yield is 73%. 1H NMR 500 MHz, (C_6D_6) δ : 3.3–1.9 (5H, br, B_{cage} -H), 1.66 (1H, s, C_{cage} -H), 1.17 (9H, s+d, Pt-Me₃, $^2J_{PtH}$ = 79.0 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2) δ : 45.10 (s, C_{cage}), 4.42 (s+d, Pt-Me₃, J_{PtC} = 714.25 Hz). $^{11}B\{^1H\}$ NMR 128.38 MHz, $(CD_2Cl_2, 25^\circ C)$ δ : 0.6 (s, 1B, Br-B opposite to carbon apex, -8.9 (s, 5B, Br-B of lower ring), -20.2 (s, 5B, H-B)). ^{11}B NMR 128.38 MHz, $(CD_2Cl_2, 25^\circ C)$ δ : 0.6 (s, 1B, Br-B opposite to carbon apex, -8.9 (s, 5B, Br-B of lower ring), -20.2 (br d, 5B, H-B, $^1J_{BH}$ = 169 Hz). All NMR data indicate an apparent three-fold rotational symmetry of the $PtMe_3$ unit and an apparent five-fold symmetry of the boranate cage, in contrast to the approximate C_s symmetry of the molecule in the crystal structure. We suggest that the $PtMe_3$ unit rapidly migrates around the (brominated) lower rim of the cage, as proposed by Weller

and co-workers (10) for rhodium(III) complexes of the same carboranate. Calcd. for $C_4H_{15}B_{11}Br_6Pt$: C 5.61, H 1.77, N 0.00; found: C 5.73, H 1.74, N not detected.

Ligand competition experiments

General considerations

All competition experiments were conducted in 1,2-dichloroethane- d_4 at room temperature (25 °C) in J. Young NMR tubes. Reactions were monitored using 1H , ^{11}B , and $^{11}B\{^1H\}$ NMR. Fluorene (unless otherwise stated) was employed as an internal standard for the fully relaxed 1H NMR with a delay time of $D_1 = 60$ s. Neat $BF_3 \cdot Et_2O$ was used as the internal reference (capillary in tube) for the ^{11}B and $^{11}B\{^1H\}$ NMR and set to 0 ppm. To increase accuracy for those competition experiments where not a solid sample (μg balance) was added but rather a liquid via 2.0 microliter syringe, 1H NMR spectral integration (with sufficient relaxation delay for the acquisition) was used in conjunction with an added internal standard (fluorene). ^{11}B NMR spectroscopy is very useful for demonstrating whether the carboranate is coordinated or not to trimethylplatinum. When the carboranate is decoordinated to some extent in an equilibrium mixture, two species are seen in the ^{11}B NMR spectrum, the coordinated species and that of the noncoordinated species. The noncoordinated species exhibits the most pronounced upfield shift on two peaks of its three-peak spectrum. The two ^{11}B peaks that shift the most on going from the coordinated to noncoordinated (or vice versa) are the peaks at the Br-*B* opposite to carbon apex and that of the lower Br-*B* ring (the peaks that contain the Me_3Pt moiety). These peaks experience an upfield shift of approximately 2.5 ppm and 1.2 ppm, respectively, when the carboranate becomes decoordinated. The third ^{11}B peak, belonging to the "upper ring" (5 BH), remains virtually unchanged (± 0.1 ppm).

Solution data for $[(closo-CB_{11}H_6Br_6)PtMe_3]$

1H NMR 400 MHz, ($CICD_2CD_2Cl$) δ : 3.4–1.5 (5H, br, B_{cage-H}), 2.98 (overlap with B_{cage-H} region, 1H, s, C_{cage-H}), 1.84 (overlap with B_{cage-H} region, 9H, s+d, Pt- Me_3 , $^2J_{PtH} = 79.3$ Hz). $^{11}B\{^1H\}$ NMR 128.38 MHz, ($CICD_2CD_2Cl$, 25 °C) δ : 0.6 (br s, 1B, Br-*B* opposite to carbon apex, -9.0 (s, 5B, Br-*B* of lower ring), -20.5 (br s, 5B, H-*B*).

Solution data for $[Cs][closo-CB_{11}H_6Br_6]$

$^{11}B\{^1H\}$ NMR 128.38 MHz, ($CICD_2CD_2Cl$, 25 °C) δ : -2.0 (br s, 1B, Br-*B* opposite to carbon apex), -10.2 (br s, 5B, Br-*B* of lower ring), -20.6 (br s, 5B, H-*B*).

Competition Experiment with Kläui Ligand (Sodium(cyclopentadienyl) tris(dimethylphosphito)cobaltate(I))

To a solution containing 1.09 mg (0.001 27 mmol) of $[(closo-CB_{11}H_6Br_6)PtMe_3]$ and 1.23 mg (0.007 40 mmol) of fluorene in 470 μL of 1,2-dichloroethane- d_4 (0.002 71 mol/L in Pt) was added the Kläui ligand ($[Na][CpCo[P(O)(OCH_3)_2]_3]$, FW: 474.1 g/mol) in approximately 0.3 to 0.4 equiv. per Pt per titrant, aided with sonication. A total of 2.08 equiv. were added. After adding 1 equiv. of Kläui ligand, the carboranate becomes fully decoordinated and a different Pt species is observed in quantitative yield in the

1H NMR. The newly formed species has a 1H NMR shift value of 0.92 ppm and $^2J_{PtH} = 78.5$ Hz, in contrast with the starting $[(closo-CB_{11}H_6Br_6)PtMe_3]$ with a chemical shift value of 1.84 ppm and $^2J_{PtH} = 79.3$ Hz. After adding more than one equiv. of ligand, the 1H displays two Kläui Cp ligand environments, namely that of the coordinated $[Me_3Pt(CpCo[P(O)(OCH_3)_2]_3)]$ at 5.15 ppm and an additional peak belonging to the Cp ligand of the free $[Na][CpCo[P(O)(OCH_3)_2]_3]$ at 5.37 ppm (28). The $^{11}B\{^1H\}$ NMR shows that the new noncoordinated species has chemical shift values similar to those of $[Cs][closo-(CB_{11}H_6Br_6)]$ in the same solvent, leading us to conclude that the noncoordinated carboranate species is $[Na][closo-(CB_{11}H_6Br_6)]$. ^{11}B spectra, internally referenced ($BF_3 \cdot Et_2O$), were also acquired, and they confirm that during the titration the amount of $[(closo-CB_{11}H_6Br_6)PtMe_3]$ decreases, whereas a new species grows in. $^{11}B\{^1H\}$ shows that peak at the Br-*B*, opposite to the carbon apex, has shifted from +0.60 ppm to -2.10 ppm on going from the coordinated to noncoordinated $closo-CB_{11}H_6Br_6^-$, while the peak at Br-*B* of the lower ring, the ring which contains the Me_3Pt^+ , shifts from -9.06 ppm to -10.36 ppm on going from the coordinated to noncoordinated $closo-CB_{11}H_6Br_6^-$, while the B-H ring peaks remain virtually unchanged at -20.51 ppm. The largest ^{11}B shifts observed are those that contain the Me_3Pt^+ bound moiety.

Competition experiment with THF

To a solution containing 1.73 mg (0.002 02 mmol) of $[(closo-CB_{11}H_6Br_6)PtMe_3]$, 2.37 mg (0.0143 mmol) of fluorene in 560 μL of 1,2-dichloroethane- d_4 (0.00361 mol/L in Pt) was added THF (peaks appear as broad singlets at 3.65 ppm and 1.79 ppm) in amounts corresponding to approximately 8 equiv. per Pt, until $closo-CB_{11}H_6Br_6^-$ becomes fully decoordinated. It is interesting to note that it required 7.9 μL (0.0974 mmol) of thf (or 48 equiv.) per Pt to fully decoordinate the carboranate. Observed is the formation of a new species, assigned as $Me_3Pt(thf)_3^+$, with a chemical shift of 1.23 ppm for the Pt-methyl and $^2J_{PtH} = 76.8$ Hz, clearly distinct from the starting $[(closo-CB_{11}H_6Br_6)PtMe_3]$ having its methyl resonance at 1.84 ppm ($^2J_{PtH} = 79.3$ Hz). The ^{11}B NMR spectrum confirms that the carboranate becomes noncoordinating, where the chemical shifts of the new species are very similar to $[Cs][closo-(CB_{11}H_6Br_6)]$ in the same solvent, which confirms the assignment as noncoordinating $closo-CB_{11}H_6Br_6^-$. The internally referenced ($BF_3 \cdot Et_2O$). The $^{11}B\{^1H\}$ NMR spectrum shows that peak at Br-*B* opposite to the carbon apex has shifted upfield 2.59 ppm to δ -2.15 ppm on going from the coordinated to noncoordinated $closo-CB_{11}H_6Br_6^-$, while the peak at Br-*B* of the lower ring, the ring which contains the Me_3Pt^+ , has shifted upfield 1.28 ppm to δ -10.25 ppm on going from the coordinated to noncoordinated $closo-CB_{11}H_6Br_6^-$, while the B-H ring peaks remains virtually unchanged at -20.60 ppm.

Competition experiment with acetone

In a similar fashion to the thf experiment, the acetone experiment was conducted. To a solution containing 1.67 mg (0.001 95 mmol) of $[(closo-CB_{11}H_6Br_6)PtMe_3]$, 1.57 mg (0.009 45 mmol) of fluorene in 560 μL of 1,2-dichloroethane- d_4 (0.003 48 mol/L in Pt) was added 5.3 μL

(0.0722 mmol) of acetone (peak appears as a singlet at 2.08 ppm), which is approximately 38 equiv. per Pt. The ^1H NMR shows a slightly broadened PtMe_3 environment at with a chemical shift value of 1.82 ppm, and a $^2J_{\text{PtH}}$ is unresolved (because of overlap of the carbon satellites of the added acetone and a broadening of the Me_3Pt peaks), compared with the starting material of chemical shift value of 1.84 ppm. The $^{11}\text{B}\{^1\text{H}\}$ spectrum shows *one species only* and is that of the starting coordinated carboranate ligand, [*closo*- $\text{CB}_{11}\text{H}_6\text{Br}_6$] PtMe_3], with slight broadening of base peaks for the two B-Br peaks directly coordinated to the Me_3Pt^+ moiety. The internally referenced ($\text{BF}_3\text{-Et}_2\text{O}$) $^{11}\text{B}\{^1\text{H}\}$ shows that the peak at Br-B opposite to the carbon apex has shifted slightly upfield 0.264 ppm to broad singlet at δ 0.25 ppm (compared with a approximately 2.6 ppm upfield shift for full decoordination experiments), while the peak at Br-B of the lower ring, the ring which contains the $[\text{Me}_3\text{Pt}]^+$, has shifted upfield 0.09 ppm to δ -9.13 ppm, while the B-H ring peaks remains virtually unchanged at -20.54 ppm). The data show that substantial decoordination of the carboranate does not occur. The very small chemical shift differences that are observed may indicate a weak outer-sphere association of acetone.

Competition experiment with NBu_4OTf

This experiment was performed using an accurate analytical mass balance with a ± 0.01 mg error. To a solution containing 1.33 mg (0.00155 mmol) of [*closo*- $\text{CB}_{11}\text{H}_6\text{Br}_6$] PtMe_3] was added 0.59 mg (0.00151 mmol, 0.97 equiv. per Pt, FW: 391.53 g/mol) of NBu_4OTf in 340 μL (0.00456 mol/L in Pt) of 1,2-dichloroethane- d_4 . The $^{11}\text{B}\{^1\text{H}\}$ spectrum shows the partial decoordination in a 43:57 ratio of coordinated-to-noncoordinated. The de-coordinated species $^{11}\text{B}\{^1\text{H}\}$ peaks appear at -2.05 ppm, -10.25 ppm, and -20.65 ppm in the given reaction conditions.

Reverse competition experiment with $[\text{Me}_3\text{Pt}(\text{acetone})_3][\text{BF}_4]$

The tris-acetone complex was prepared using modified literature methods (11, 29), similar to the preparation of $[\text{Me}_3\text{Pt}(\text{benzaldehyde})_3][\text{BF}_4]$ but using acetone instead of benzaldehyde and using 1,2-dichloroethane- d_4 instead of dichloromethane- d_2 solvent. ^1H NMR 400 MHz, ($\text{ClCD}_2\text{CD}_2\text{Cl}$) δ : 2.24 (18H, s), 1.48 (9H, s+d, Pt-Me₃, $^2J_{\text{PtH}} = 79.8$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR 128.38 MHz, ($\text{ClCD}_2\text{CD}_2\text{Cl}$, 25 °C) δ : -1.52 (s, 1B, BF_4). Titrating in 0.21 to 1.87 equiv. of $[\text{Cs}][\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$ into a 420 μL solution of 1,2-dichloroethane- d_4 (0.0227 mol/L in Pt) containing 4.77 mg (0.00952 mmol) of $[\text{Me}_3\text{Pt}(\text{acetone})_3][\text{BF}_4]$ (FW: 501.23 g/mol), partial decoordination of the acetone complex occurs as shown by the ^1H NMR shift of acetone moving upfield from 2.24 ppm to 2.10 ppm. A new Me_3Pt species at 1.78 ppm, appears downfield from the starting species. Due to the relative broadness of the Pt satellites, it is difficult to accurately assess the $^2J_{\text{PtH}}$. Also formed is an insoluble precipitate, consistent with a reaction forming insoluble CsBF_4 . The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows the disappearance of the sharp BF_4 peak at or near the equivalence point of Cs salt addition. Despite the broadened nature of the $^{11}\text{B}\{^1\text{H}\}$ spectrum, it shows that there are two *distinct* species present in solution at the 1.8 equivalence point, assigned as [*closo*-

$\text{CB}_{11}\text{H}_6\text{Br}_6$] PtMe_3] at $^{11}\text{B}\{^1\text{H}\}$ } 0.1 ppm, -9.32 ppm, and -20.48 ppm, as well as free, excess $[\text{Cs}][\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$ at -2.02 ppm, -10.17 ppm, and -20.48 ppm.

Crystallography³

The crystal was refined as a non-merohedral twin with the ratio of the twin components refining to 0.818(2):182(2). In addition, a large electron density peak located in the final difference Fourier map refined to the equivalent of ca. 5% of a Pt atom. Hence the structure was refined as containing "whole molecule disorder" with only the Pt atom being refined over two sites. The refined occupancies of the maximum and minimum components are 0.951(3) and 0.049(3). All other atoms were refined with full occupancy.

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28. It seems that, aided by the relative nonpolarity of the NMR solvent, the excess Kläui ligand ([Na][CpCo[P(O)(OCH₃)₂]₃]) present after more than 1 equiv. (relative to Pt) has been added, partially associates with the “free” Na⁺ of the [Na][*closo*-(CB₁₁H₆Br₆)] in the titration solution. This results in a slight downfield shift (by 0.36 ppm) of the Cp protons in such excess Kläui ligand, where the resonance is observed at 5.36 ppm as opposed to the 5.00 ppm value observed for the pure ligand [Na][CpCo[P(O)(OCH₃)₂]₃] in the same solvent. Solution data of Kläui ligand, ([Na][CpCo[P(O)(OCH₃)₂]₃], in the absence of extra sodium: ¹H NMR 400 MHz, (ClCD₂CD₂Cl) δ: 5.00 (5H, s, Cp ligand), 3.54 (18H, dd, J_{HH} = 3.8, 6.5 Hz).
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