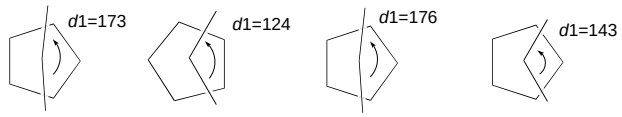
pyramidal geometries known for the singlet state of d^6 [$CpML_2$] and [CpMLX] systems may actually belong to two distinct electronic states, rather than being the result of pseudo Jahn–Teller distortions in the same electronic state as previously proposed.[6, 21] Indeed, by altering the occupancy of the d^6 electrons in [$CpMn(CO)_2$] (**5**) we located a nearly planar bound stationary state (**5**-^{1}A′b, Figure 6),[22] 167 kJ mol^{-1} above the pyramidal structure (**5**-^{1}A′a). More



5-^{1}A'a	**5**-^{1}A'b	**5**-^{3}A'	**5**-^{3}A"
$(a')^2(a')^2(a')^2$	$(a')^2(a')^2(a'')^2$	$(a')^2(a'')^2(a')^1(a')^1$	$(a')^2(a')^2(a')^1(a'')^1$
E_{rel} = 198	E_{rel} = 31.4	E_{rel} = 0.0	E_{rel} = 14.5

Figure 6. Angular parameters (in degrees), occupancy of the d^6 electrons, and relative energy (in kJ mol^{-1}) of the low-lying singlet and triplet states of [$CpMn(CO)_2$].

importantly, extension of the given argument to the triplet state of **5** affords two minima (**5**-^{3}A′ and **5**-^{3}A″, Figure 6), both of which are *lower* in energy than **5**-^{1}A′a. Calculated frequencies of **5** have been invoked in the past to aid the characterization of transient intermediates observed in the photolysis of [$CpMn(CO)_3$],[7b] but only one triplet species was accounted for.

In conclusion, results from the present study reveal that both the singlet and triplet low-energy states of the unsaturated [$CpML_3$] system are subject Jahn–Teller effects. This finding can provide a basis for interpreting the geometries in other unsaturated [$CpML_n$] compounds, and suggests a need to consider more than one state in electronic structure studies of related systems.

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Remarkable Boosting of the Binding of Ion-Paired Organic Salts by Binary Host Systems**

Grazia Cafeo, Giuseppe Gattuso, Franz H. Kohnke, Anna Notti, Salvatore Occhipinti, Sebastiano Pappalardo, and Melchiorre F. Parisi*

The formation of host–guest complexes is normally achieved by the combined action of a number of weak noncovalent forces between the binding sites of the receptor and the target substrate.[1] However, for host–guest complex-

[*] Prof. M. F. Parisi, Dr. G. Cafeo, Dr. G. Gattuso, Prof. F. H. Kohnke, Dr. A. Notti
Dipartimento di Chimica Organica e Biologica
Università di Messina
Salita Sperone 31, 98166 Messina (Italy)
Fax: (+39) 090-393-895
E-mail: mparisi@unime.it
Prof. S. Occhipinti, Prof. S. Pappalardo
Dipartimento di Scienze Chimiche
Università di Catania
Viale A.Prof. Doria 6
95125 Catania, Italy

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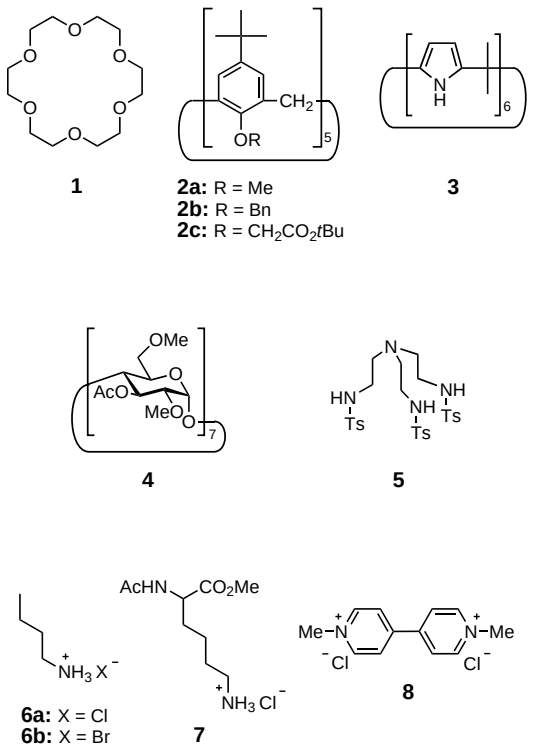
ation to occur, complementarity of binding sites is not the only requirement, since other factors, such as solvation, conformational changes, and in the case of charged species, the interference arising from ion-pairing effects, must concur for the process to have an overall favorable free energy.[2] Counterions also play a crucial role in the binding of charged species by neutral receptors.[3]

Ion-pair recognition, namely the simultaneous complexation of the cationic and anionic guest species, is a current challenge in host–guest and supramolecular chemistry. To this end, heterotopic receptors have been designed which take advantage of cooperative and allosteric effects.[3b, 4] Although these systems show undeniable potential for the binding of targeted ion pairs (including zwitterionic molecules),[5] an efficient assembly of cation and anion binding sites onto three-dimensional molecular platforms requires laborious multistep syntheses and careful control of the conformation. As an alternative, a combination of synthetically more-accessible anion and cation receptors (dual-host approach) has recently been used in membrane transport and extraction of inorganic salts,[6] but the mutual contributions to the overall binding process have been scarcely investigated. In the present study we demonstrate that when suitably chosen pairs of neutral receptors are used for the complexation of organic salts in apolar solvents, they exhibit a remarkable synergic effect which causes a dramatic enhancement of the binding ability of each host component towards its "complementary ion".

Scheme 1 shows the various neutral hosts employed in this study, which include [18]crown-6 (**1**), *p-tert*-butylcalix[5]-arenes with various degrees of preorganization **2a**–**c**,[7] calix[6]pyrrole (**3**),[8] per-(2,6-*O*-dimethyl-3-*O*-acetyl)-β-cyclodextrin (**4**),[9] and trisulfonamide **5**.[10] The mutual effect of appropriate pairs of cation/anion receptors in the binding of selected organic salts (*n*-butylammonium halides **6a**, **b**, N^{α}-acetyl-L-lysine methyl ester hydrochloride (**7**), methyl viologen dichloride (paraquat dichloride, **8**)) was investigated by ^{1}H NMR complexation experiments in CD_2Cl_2. The synergic effect that results in an increased binding ability of each host towards its complementary ion was evaluated by comparison with the degree of complexation observed when each host was used individually.



Scheme 1. Hosts and guests studied.

First of all we investigated the complexation of nBuNH$_3^+$Cl$^-$ (**6a**) with **1** and **3**. Calix[6]pyrrole (**3**) is known to form 1:1 complexes with halides in both the solid state and in solution, with a preference for chloride ions.[8b,c] When a solution of **3** (5×10^{-3} M) in CD_2Cl_2 is subjected to **6a** (0.5 equiv), only a weak host–guest interaction occurs, as evidenced by the small downfield shift experienced by the pyrrole NH resonance. This result is consistent with a fast complexation process of Cl$^-$ ions on the NMR timescale. However, the process becomes slow upon addition of **1** (1 equiv) to this mixture, and separate signals for the free and complexed **3** appear in the spectrum. The simultaneous complexation of nBuNH$_3^+$ ions by **1** (tripodal hydrogen bonding with the ethereal oxygen atoms, broad signal at $\delta =$ 7.21 ppm) causes a weakening of the ion pair, and greatly facilitates the uptake of chloride ions by **3**. Further addition of **6a** so as to reach a 1:1:1 ratio of the three components (**3**:**1**:**6a**), produces a single detectable species by NMR spectroscopy, that is, a supramolecular system consisting of a supercation (nBuNH$_3^+ \subset$ **1**, namely, the cation is H-bonded to the crown ether) and a superanion (Cl$^- \subset$ **3**, the anion is H-bonded to six pyrrole NH protons). This observation implies there is a nearly 100% complexation of Cl$^-$ ions by the moderate anion receptor **3** in the presence of an equimolar amount of **1**.

To further prove and quantify the synergism of appropriate binary host systems in the binding of **6a**,**b**, we next replaced the shape-unselective host **1** with three-dimensional *p-tert*-butylcalix[5]arenes **2a**–**c** as the cation receptors, which are known to selectively form 1:1 inclusion complexes with linear alkyl ammonium ions.[11] When a solution of the highly flexible **2a** in CD_2Cl_2 is exposed to **6a** (1 equiv), a doubling of the signals for the free and complexed host and guest species is observed, but less than 2% of the inclusion complex is formed. Although **2a** alone shows a very poor affinity for the nBuNH$_3^+$ ion, after the addition of the anion receptor **3** (1 equiv) the signals of the free guest disappear, while those of the included nBuNH$_3^+$ ion show up in the characteristic high-field region of the spectrum ($\delta = -0.4$ to -2.0 ppm).[11] Simultaneously, the counteranion (Cl$^-$) is completely complexed by **3**, as evidenced by the shift of the pyrrole NH resonance from $\delta = 7.74$ (free host) to $\delta = 10.91$ ppm (complex). This result confirms that the conversion into the supramolecular system (that is, the supercation (nBuNH$_3^+ \subset$ **2a**) and the superanion (Cl$^- \subset$ **3**)) is close to 100%. As in the previous case, a weak nonpreorganized receptor **2a** is transformed into a powerful one by the synergic action of a "complementary" receptor such as **3**.

The boosting of the binding affinities of the various calix[5]arene/calix[6]pyrrole pairs for *n*-butylammonium hal-

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ides **6** in CD_2Cl_2 and the relevant synergic factors are shown in Table 1. The complexation processes are generally slow on the NMR timescale.[12, 13] Thus, conditional association constants of the cationic (C) and anionic (A) receptors for their complementary ions ($K(C)_2$ and $K(A)_3$, respectively) and the corresponding conditional association constants observed in the presence of each other ($K(C)_{2+3}$ and $K(A)_{2+3}$) could be determined by direct analysis of the spectra. Although errors are inherent in the NMR technique for a degree of complexation outside the range 20–80%,[14] in those cases where an apparent >99% complexation was observed the K values were estimated by assuming a degree of complexation not higher than 95–98%. With this in mind, the synergic factors (computed as the ratio $K(C)_{2+3}/K(C)_2$ and $K(A)_{2+3}/K(A)_3$) are probably underestimates.

A scrutiny of Table 1 shows that, as expected, $K(C)_2$ and $K(C)_{2+3}$ for the binding of the nBuNH$_3^+$ ion depends on the degree of preorganization of the cation receptor (more preorganized hosts give higher values) and the "softness" of the counterion. The very high $K(C)_{2+3}$ values estimated for the binding of **6a**, **b** by the pair **2c** + **3** are in good agreement with the value earlier reported for the binding of the picrate salt of nBuNH$_3^+$ by **2c** ($\lg K = 6.47$, determined by UV spectroscopy in $CHCl_3$).[11a] Likewise, $K(A)_3$ values are in accord with the better size-matching of Cl^- ions for the calixpyrrole cavity. The computed synergic factors show that the binding of **6** by the binary system **2** + **3** are, in many cases, as high as 10^3–10^4 relative to **2** or **3** alone. The level of this synergic effect is similar to the increase in the cation binding affinity of the anion complexes of certain cyclic peptides.[4e] The synergic factors for the binding of **6b** are lower than those for **6a**. This observation is easily explained both by the higher $K(C)_2$ value for **6b** and by the lower affinity of **3** for Br^- ions.

This finding emphasizes the concept that pairs of receptors must be carefully chosen for optimum binding of a target ion-paired guest. Accordingly, the synergic factor in the binding of **6a**, **b** by combinations of **2a**–**c** with the C_3-symmetric anion receptor **5** (designed for tetrahedral rather than spherical anion complexation)[10] does not exceed five. Furthermore, it should be pointed out that the increased binding efficiency of these binary host systems does not in any way affect the intrinsic selectivity of each of the two host components.[15]

The latter point is of particular interest in view of possible applications in the biochemical, environmental, and analytical fields. For example, the highly preorganized calix[5]arene **2c** has recently been proposed as a potential biomimetic host for some biologically important ammonium substrates, such as N^{α}-acetyl-L-lysine methyl ester hydrochloride (**7**).[11a] One of the main problems in complexing these organic salts in nonpolar solvents is their tight ion pairing and their extremely low solubility in these media.[16] When a 1:1:1 mixture of **2c**, **3**, and **7** in CD_2Cl_2 is sonicated, the ammonium salt slowly dissolves as a result of the simultaneous complexation of the cationic and anionic components of the guest by the respective receptors. The formation of the supramolecular system is confirmed by ^{1}H NMR spectroscopic analysis, with the extent of complexation being close to 100% (Figure 1). The spectrum does not change after tenfold dilution.

The versatility and effectiveness of this approach was further confirmed by the complexation of the known herbicide paraquat dichloride (**8**) by the use of **3** in conjunction with β-cyclodextrin **4** in CD_2Cl_2. Receptor **4** is known to complex paraquat (preferably as the hexafluorophosphate salt) in polar solvents (CH_3CN, acetone).[17] However, **8**, which is sparingly soluble in a solution of CD_2Cl_2 containing one equivalent of **4**, is mostly dissolved (80%) when two equivalents of **3** are also present. The ^{1}H NMR spectrum is once again consistent with the formation of the expected supramolecular system (paraquat $\subset$ **4** supercation and $Cl^- \subset$ **3** superanion).

Since it is known that water lowers the anion binding ability of calix[6]pyrrole (**3**),[8c] we tested whether such action could be so pronounced as to produce a detectable decrease in the synergic effect. The binding of **6a** by the less effective pair of receptors (**2a** + **3**) decreased from 90 to 75% in water-saturated CD_2Cl_2. However, no significant decrease was observed with the most effective pairs of receptors.

In conclusion, we have demonstrated that effective binding of targeted ion-paired organic salts can be achieved by a suitable combination of cationic and anionic receptors. The observed synergic factors (up to 10^4) can be ascribed to the cleavage of the ion pair by the combined action of the two receptors. As a result of the negligible electrostatic interaction between the charged components of the salt when confined in the cavity of their complementary host the conditional association constants measurable by this approach may be regarded as close to those expected in an ideal case where the counterion is absent.

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Table 1. Conditional association constants [M^{-1}] for the formation of 1:1 n-butylammonium halide complexes with receptors **2** and/or **3** (taken individually or as 1:1 pairs) and calculated synergic factors.[a,b]

Pairs	Salt	$K(C)_2$	$K(C)_{2+3}$	$K(C)_{2+3}/K(C)_2$	$K(A)_3$	$K(A)_{2+3}$	$K(A)_{2+3}/K(A)_3$
2a + **3**	nBuNH$_3^+$Cl$^-$	<5	$>7.6\times10^4$	$>1.5\times10^4$	<10	$>7.6\times10^4$	$>7.6\times10^3$
2b + **3**	nBuNH$_3^+$Cl$^-$	<10	$>2\times10^5$	$>2\times10^4$	<10	$>2\times10^5$	$>2\times10^4$
2c + **3**	nBuNH$_3^+$Cl$^-$	504[c]	$>2\times10^7$	$>2\times10^4$	<10	$>2\times10^5$	$>2\times10^4$
2a + **3**	nBuNH$_3^+$Br$^-$	24[c]	160[c]	6.7	<5	180[c]	>36
2b + **3**	nBuNH$_3^+$Br$^-$	128[c]	1750[c]	13.7	<5	1670[c]	>330
2c + **3**	nBuNH$_3^+$Br$^-$	$>1.6\times10^4$	$>2\times10^7$	$>1.2\times10^3$	<5	1.4×10^4	$>2.8\times10^3$

[a] By ^{1}H NMR complexation experiments of equimolar 5×10^{-3} M solutions of the three components in CD_2Cl_2 at 293 K. [b] See text for the definition of column headings. [c] Estimated error = 10%.

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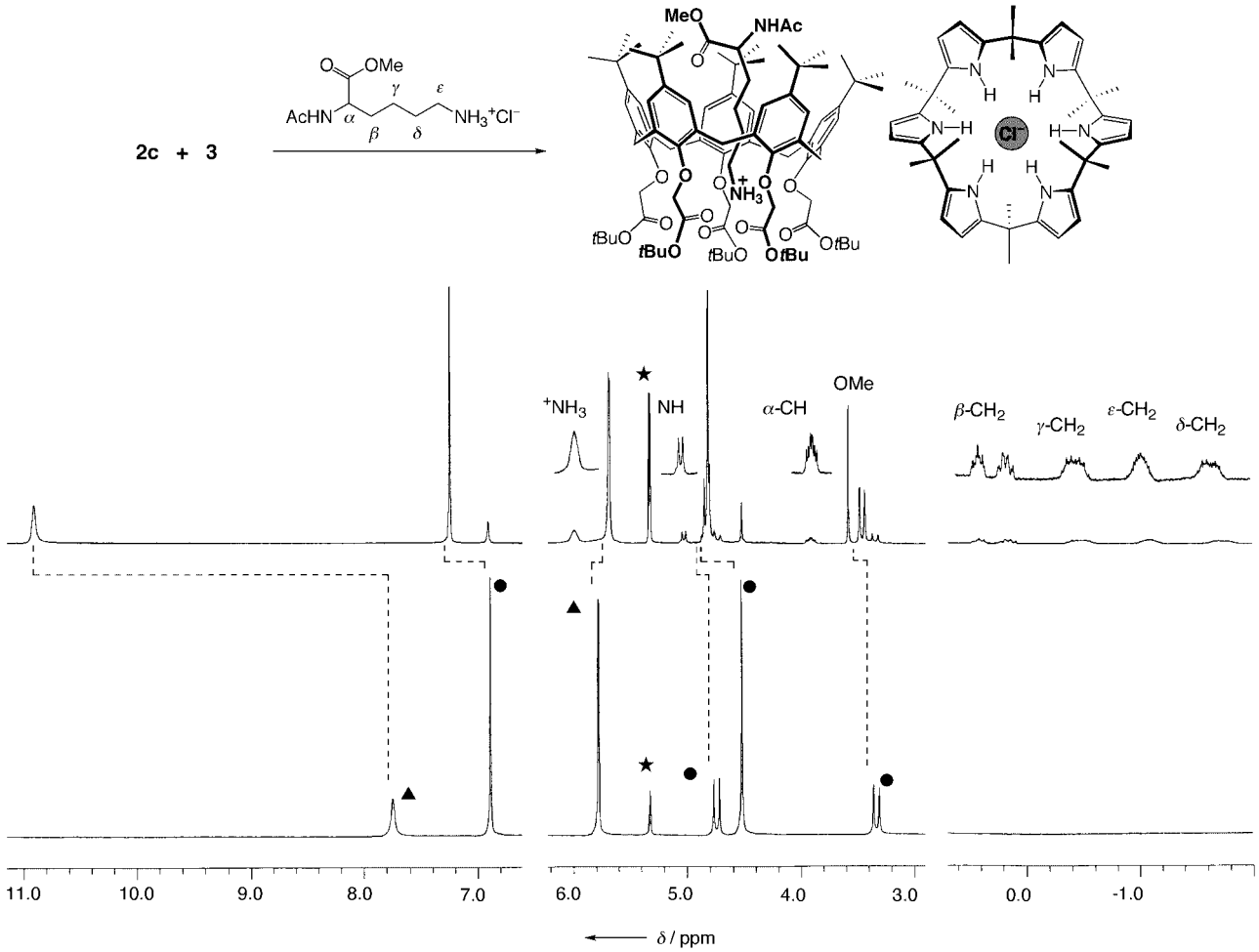

Figure 1. Selected regions of the ^{1}H NMR spectra (300 MHz, CD_2Cl_2, 293 K) of the 1:1 binary host system **2c** + **3** (bottom), and formation of the supercation N^{α}-Ac-L-Lys-OMe · H^+ ⊂ **2c** and superanion Cl^- ⊂ **3** (top) after addition of solid **7** (1 equiv). Insets (top trace) refer to the resonances of the cation included in the calix[5]arene cavity. Symbols ▲, ●, and ★ indicate the calix[6]pyrrole, calix[5]arene, and residual solvent resonances, respectively.

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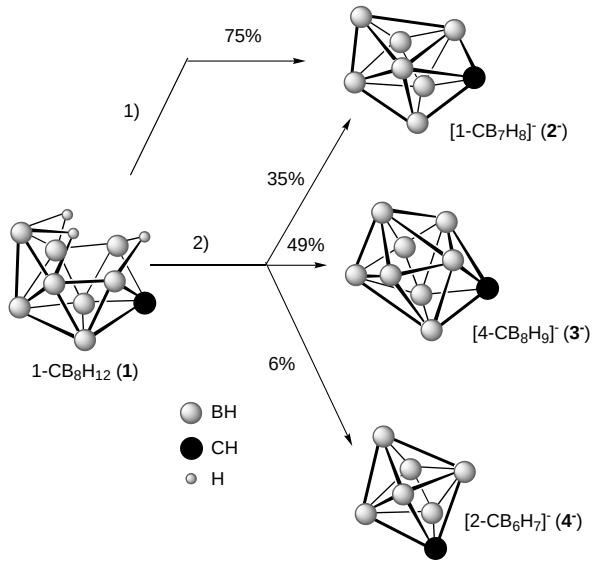
The [*closo*-2-CB_6H_7]$^-$ Ion: The First Representative of the 7-Vertex Monocarbaborane Series**

Bohumil Štíbr,* Oleg L. Tok, Wolfgang Milius, Mario Bakardjiev, Josef Holub, Drahomír Hnyk, and Bernd Wrackmeyer

In contrast to the extensively explored area of dicarbaborane chemistry,[1] that of monocarbaboranes is much less represented, and many of the fundamental cluster types, namely those of the *nido* and *arachno* series, are unreported as yet. A typical and relatively well-developed field of monocarbaborane chemistry is that of the classically *closo* monocarbaborane anions of general formula [CB_nH_{n+1}]$^-$. Of these anions, thanks also to the recent discoveries of the [CB_7H_8]$^-$ and [CB_8H_9]$^-$ ions[2, 3] a complete series from $n = 7$ to 12 has already been isolated and structurally characterized, together with the 6-vertex ion [CB_5H_6]$^-$ and its conjugated acid CB_5H_7.[4] Nevertheless, the 7-vertex ion [CB_6H_7]$^-$ has so far remained elusive. At present, most studies in the area of *closo* monocarbaboranes focus on the substitution chemistry of the [CB_9H_{10}]$^-$ and [$CB_{11}H_{12}$]$^-$ ions.[1, 5] Currently, these anions attract much attention as so-called weakly coordinating anions because of their very low Lewis basicities.[6] Moreover, *closo* monocarbaboranes are studied as starting materials for borane-based liquid crystals.[7] We now report preliminary results on the isolation and structural characterization of the [CB_6H_7]$^-$ ion, a missing member of the 7-vertex *closo* monocarbaborane series.

Under strictly anaerobic conditions (deoxygenated Ar), the reaction between *nido*-1-CB_8H_{12} (**1**)[8] and two equivalents of Et_3N in dry toluene (reflux, 24 h) resulted in the isolation of previously reported[2] anion [*closo*-1-CB_7H_8]$^-$ (**2**$^-$), yield 75% [Eq. (1); Scheme 1 (path 1)].

$$\underset{\mathbf{1}}{1\text{-}CB_8H_{12}} + 2\,Et_3N \rightarrow \underset{(\mathbf{2}^-Et_3NH^+)}{[Et_3NH]^+[1\text{-}CB_7H_8]^-} + Et_3N{\cdot}BH_3 \qquad (1)$$



Scheme 1.

In contrast, the reaction products are entirely different when the same reaction is carried out in an atmosphere containing N_2 with approximately 5% O_2 (Scheme 1, path 2)). The reaction then afforded a mixture of the known ions **2**$^-$ and [*closo*-4-CB_8H_9]$^-$ (**3**$^-$), together with a new ion [2-CB_6H_7]$^-$ (**4**$^-$; yields 35, 49, and 6%, respectively). Anion **4**$^-$ was finally isolated as a PPh_4^+ salt (**4**$^-$ PPh_4^+) by preparative TLC. The formation of **4**$^-$ seems to be in agreement with the side reaction given in Equation (2) and is consistent with the elimination of two BH vertices from structure **1**.

$$\underset{\mathbf{1}}{1\text{-}CB_8H_{12}} + 2\,Et_3N + O_2 + H_2O \rightarrow \underset{(\mathbf{4}^-Et_3NH^+)}{[Et_3NH]^+[2\text{-}CB_6H_7]^-} + Et_3N{\cdot}BH_3 + B(OH)_3 \qquad (2)$$

Iodination of **4**$^-$ PPh_4^+ with I_2 (molar ratio 1:2.1) in CH_2Cl_2 in the presence of NEt_3 (HI scavenger) at ambient temperature resulted in the isolation of the diiododerivative [4,5-I_2-*closo*-2-CB_6H_5]$^-$[PPh_4]$^+$ (4,5-I_2-**4**$^-$ PPh_4^+) in 93% yield.

[*] Prof. Dr. B. Štíbr,[+] Dr. M. Bakardjiev, Dr. J. Holub, Dr. D. Hnyk
Institute of Inorganic Chemistry
Academy of Sciences of the Czech Republic
25068 Řež (the Czech Republic)
Research Centre for New Inorganic Compounds and Advanced Materials, University of Pardubice
Fax: (+42) 0220941502
E-mail: stibr@iic.cas.cz
Dr. O. L. Tok, Dr. W. Milius, Prof. Dr. B. Wrackmeyer
Laboratorium für Anorganische Chemie der Universität Bayreuth
Postfach 101251, Bayreuth, Bayern 95440 (Germany)
[+] Laboratorium für Anorganische Chemie der Universität Bayreuth
Postfach 101251, Bayreuth, Bayern 95440 (Germany)

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