Metal-Ion-Templated Polymers:

Synthesis and Structure of N-(4-Vinylbenzyl)-1,4,7-Triazacyclononanezinc(II) Complexes, Their Copolymerization with Divinylbenzene, and Metal-Ion Selectivity Studies of the Demetalated Resins—Evidence for a Sandwich Complex in the Polymer Matrix**

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The innovative studies of Wulff, Mosbach, and Shea, among others,^[1] introduced and further developed the concept of templated polymers, which initially involves a host-guest relationship between a vinyl monomer host and a bound guest acting as a template. This host-guest complex is then polymerized with a cross-linking agent, which then provides spatially regulated sites in the polymer matrix and, it is hoped, further allows continual recognition of the removable guest (the template) in subsequent reintroduction experiments. One of the types of guest templates utilized in this elegant approach to highly selective polymers of defined architecture was metal ions.^[2] However, metal-ion-imprinted polymers have received much less attention than polymers imprinted with organic compounds; the following aspects, for example, need to be addressed: 1) the unequivocal structures of the complexes between the vinyl monomer as ligand and the metal ion; 2) polymerization parameters such as the effect of the metal ion, ligand structure, and the nature of the cross-linking agent; 3) the structure of the imprinted metal-ion site in the polymer; and 4) whether subsequent selectivity is a consequence of the metal-ion recognition process or the thermodynamic stability of the (polymeric ligand)-(metal ion) complex.

Recently we have been developing an environmental inorganic chemistry program that focused on polymer-pendant ligands that were designed from biomimetic or specific heteroatom concepts for selective metal ion complexation.^[3] These studies were successful in providing modified 6% cross-linked divinylbenzene-polystyrene beads with anchored ligands that were selective in removing a variety of metal ions from aqueous solution. However, one important goal of our program was to develop polymers that were highly selective to certain divalent metal ions (such as Cu^{2+}) in the presence of trivalent metal ions (for example Fe³⁺, a ubiquitous metal ion found in many aqueous environmental solutions).

In this communication, we report on our initial results in the new, exciting field of metal-ion-templated polymers. We define a novel system highly selective to Cu^{2+} ions in the presence of Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and Mn^{2+} ions, which contains the well-known 1,4,7-triazacyclononane (TACN) ligand.^[4]

The synthesis of the 4-vinylbenzyl-substituted TACN ligands 1 and 2 was readily accomplished in high yields by treating 1 or 3 moles of 4-vinylbenzyl chloride with TACN, and their struc-

[*] Dr. R. H. Fish, Dr. H. Chen, Dr. R. L. Albright, Dr. J. Devenyi Lawrence Berkeley National Laboratory University of California Berkeley, California 94720 (USA) Fax: Int. code + (510)486-5401 e-mail: rhfish@lbl.gov Dr. M. M. Olmstead Department of Chemistry, University of California, Davis (USA)

[**] The studies at LBNL were generously supported by the Office of Environmental Management, Office of Science and Technology, Office of Technology Systems, Efficient Separations and Processing Cross Cutting Program under the U. S. Department of Energy Contract No. DE-ACO3-76SF00098. tures were assigned on the basis of ¹H NMR spectroscopy, FAB-MS, and elemental analysis (see Experimental Section). The Zn^{2+} complexes 3 and 4 from 1 and 2, respectively, were



 $3 = [1-Zn](NO_3)_2$

4 = [2-Zn](NO₃)₂

prepared by reaction with $Zn(NO_3)_2$ in methanol; the unequivocal structure of complex 4 was determined by single crystal X-ray analysis (Figure 1). What is pertinent about the structure



Figure 1. Structure of 4 (the uncoordinated NO_3^- counterion was omitted). Selected bond lengths [Å] and angles [°]: Zn-N1 2.128(4), Zn-N2 2.227(4), Zn-N3 2.094(4), Zn-O1 2.109(4), Zn-O2 2.150(4), Zn-O3 2.193(4), O2-N4 1.268(6), O3-N4 1.269(6), O4-N4 1.232(6); N1-Zn-N2 82.8(2), N1-Zn-N3 86.9(2), N2-Zn-N3 84.4(2).

of complex **4** is the distorted octahedral configuration around the Zn^{2+} center and the coordination of nitrate and methanol groups that apparently prevents the formation of a possible 2:1 TACN: Zn^{2+} sandwich complex.^[5] In addition, we assign to complex **3** a similar structure to **4**, based on the analytical and spectroscopic data obtained for each complex; in solution, the FAB-MS for **3** and **4** also provide evidence for their 1:1 Zn:TACN structures.

The copolymerization of Zn^{2+} complexes 3 and 4 with the cross-linking agent DVB (80% divinylbenzene) on use of AIBN as initiator provided highly cross-linked, macroporous polymers 5 and 6 with a ratio of 1: DVB or 2: DVB of approximately 1:2.5-1:3.0 and a TACN content of 1.33 and 1.15 mmolg⁻ respectively. More importantly, the ratio of TACN: Zn²⁺ in both polymers 5 and 6 was 2:1—clear evidence that free Zn^{2+} ions were extruded during the polymerization process (loss of Zn^{2+} : in 5 43%; in 6 50%) possibly to provide a TACN-Zn²⁺ sandwich complex in the polymer matrix (Scheme 1). It is also important to note that preparation of the corresponding Cu^{2+} complexes of 1 and 2 and subsequent attempts to polymerize the resulting Cu²⁺ monomers under similar conditions to those described for 3 and 4 were not successful, due presumably to electron transfer from the developing carbon radical to the Cu^{2+} ion, which quenched or terminated the propagation step of the free radical chain reaction.^[2a] Moreover, attempts to prepare an untemplated polymer with 1 and divinylbenzene un-



Scheme 1. The Zn^{2+} sandwich complex, whose formation is postulated in the synthesis of the polymer 5.

der similar conditions to those described for 3 in order to compare its metal-ion selectivity with that of polymer 5, were unfortunately unsuccessful, since no polymeric material formed. This latter result confirms the unique role of the metal-ion template in the kinetics of the polymerization process.^[2a]

To provide further evidence for the formation of a templated, polymeric sandwich complex during polymerization reactions of **3** and **4**, we synthesized the monomeric sandwich complex **7** (see Experimental Section), which we characterized by ¹H NMR spectroscopy, mass spectrometry, and elemental analysis. Subsequent formation of polymer **5'** (TACN content 1.33 mmol g⁻¹) from **7** with DVB under similar polymerization conditions to those described for **3** and **4** clearly showed minor loss of Zn^{2+} metal ions (<15%) and the expected 2:1 ratio of TACN: Zn^{2+} in the polymer matrix (Eq. 1). This result further



substantiates the formation of the 2:1 TACN: Zn^{2+} sandwich complexes in the polymer matrices of **5** and **6**, possibly on thermodynamic grounds, and represents, to our knowledge, the first confirmation of the formation of sandwich complexes during the polymerization process in the synthesis of metal-ion-templated polymers.^[2]

The Zn^{2+} -templated polymers 5, 5', and 6, were treated with 6N HCl at ambient temperature, which provided the facile and total removal (>99%) of the Zn^{2+} template ions. Selectivity studies were carried out with the these Zn^{2+} -demetalized polymers, designated as 8, 8', and 9, respectively, to answer the question whether the more important parameter for the introduction was templating or the thermodynamic stability in the ensuing reintroduction of various metal ions into the spatially regulated sandwich arrangement of TACN ligands (Scheme 2).

We therefore performed competition experiments with the original Zn^{2+} ion template and the divalent metal ions, Cu^{2+} , Co^{2+} , Ni^{2+} , and Mn^{2+} using polymers **8**, **8'**, and **9** at pH 4.5. Table 1 shows the results: the thermodynamic stability of the newly formed $[M("TACN")_2]^{2+}$ complexes appears to dominate over imprinting; that is, the Cu^{2+}/Zn^{2+} selectivity ratio for





Scheme 2. Postulated arrangement of the TACN ligands in the demetalated polymers 8 and 8'.

Table 1. Selectivities of polymers 8, 8', and 9 for Zn^{2+} , Cu^{2^-} , Co^{2^+} , Ni^{2^+} , and Mn^{2^+} ions at pH 4.5, and Cu^{2^+} and Fe^{3^+} at pH 2.0. The values reported represent concentration as wt% and in parentheses as μ mol per g of resin of metal ion on the resin after reaction [a], as well as the relative selectivity with respect to the selected pair of ions.

	Polymer 8	Polymer 8'	Polymer 9
Cu ²⁺	7.5 (1180)	4.4 (690)	0.77 (121)
Ni ²⁺	0.05 (8.5)	0.03 (5)	0.002 (0.34)
Co ²⁺	1.0 (150)	0.78 (130)	0.002 (0.34)
Mn ²⁺	0.05 (9.0)	0.018 (3)	0.002 (0.36)
Zn ²⁺	0.05 (7.5)	0.04 (6)	0.02 (3)
$Cu^{2+}:Zn^{2+}$	157:1	115:1	7:1
Ni ²⁺	0.3 (51)	0.64 (108)	0.01 (1.7)
Co ²⁺	0.7 (120)	0.66 (114)	0.005 (0.85)
Mn ^{2 +}	0.1 (18)	0.02 (3.6)	0.005 (0.91)
Zn ^{2 +}	3 (460)	2 (306)	0.09 (13.8)
Zn ²⁺ :Ni ²⁺	9:1	3:1	8:1
Cu ²⁺	1.8 (280)	1.5 (240)	0.03 (4.7)
Fe ³⁺	< 0.01 (< 1.8)	0.006 (1.0)	0.01 (1.8)
Cu ²⁺ :Fe ³⁺	>44:1	240:1	3:1

[a] For the first two series of ions, 6 mg of resin was suspended with stirring in a 10 mL solution (pH 4.5) of a mixture of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} ions (0.04*m* each) for 18 h at ambient temperature. The resin was then washed (H₂O, MeOH), dried (ambient and under vacuum), and analyzed for metal ion concentration by X-ray fluorescence. For the third series, 6 mg of resin was suspended with stirring in a 8 mL solution (pH 2.0) of a mixture of Fe³⁺ and Cu²⁺ ions (0.02*m* each) for 18 h at ambient temperature. Workup and evaluation was as for the first two series.

8 is approximately 157:1, for 8' 115:1, and for 9 7:1. The overall order of metal-ion selectivity for all three polymers (8, 8', and partly for 9) is $Mn^{2+} \le Ni^{2+} \le Zn^{2+} < Co^{2+} < < Cu^{2+}$, which somewhat, but not exactly, follows the Irving– Williams order of stability.^[6] It is interesting to note that if at pH 4.5 the Zn^{2+} ion competes with Co^{2+} , Ni^{2+} , and Mn^{2+} , *in the absence* of Cu^{2+} , for sites in polymers 8 and 8', the overall order is: $Mn^{2+} < Ni^{2+} < Co^{2+} < < Zn^{2+}$ (Table 1); in this case, if the Irving–Williams order is also of significance for metal-ion-templated polymers, imprinting appears more important than stability.^[6] More importantly, the stability constants for the formation of the [M("TACN")₂]ⁿ⁺ complexes decrease in the order $Co^{2+} > Ni^{2+} > Zn^{2+}$ and further support the dominance of the imprinting effect of Zn^{2+} in the absence of Cu^{2-} .^[4]

We also studied the competition between Cu^{2+} and Fe^{3+} at pH 2.0, in order to test the possible selectivity of a divalent over a trivalent metal ion. From data in Table 1, the Cu^{2+} : Fe^{3+} ion selectivity is calculated to be greater than 44:1 and 240:1 and the ratio of the equilibrium selectivity coefficients ($K_{\text{Cu}^{2+}}/K_{\text{Fe}^{3+}}$) to be 3×10^5 and 7×10^5 for polymers 8 and 8', respectively, whereas polymer 9 had a low selectivity ratio of 3:1 ($K_{\text{Cu}^{2+}}/K_{\text{Fe}^{3+}} = 1.5$). These exciting results demonstrate a surprisingly high selectivity for a divalent over a trivalent metal ion and might imply that one factor in imprinted metal-ion selectivity is

the ionic radius of the original metal-ion template (Zn²⁺, 0.69 Å; Cu^{2+} , 0.72 Å; and Fe³⁺, 0.53 Å); this order of selectivity $(Cu^{2+} > > Fe^{3+})$ is diametrically opposite to that found for the bond strengths of known $[M(TACN)_2]^{n+}$ (n = 2.3) complexes as studied by X-ray crystallographic and infrared techniques $(Fe^{2+} > Co^{2+} > Fe^{3+} > Cr^{3+} > > Ni^{2+} > Cu^{2+} > Zn^{2+});$ however, more examples have to be studied before this ionic radius concept can be proven unequivocally.^[7] What is also apparent from the results in Table 1 is that even though polymer 8 and 8' were prepared from different Zn^{2+} monomer precursors (3 and 7), they provide very similar metal-ion selectivity orders and metal-ion capacities upon reintroduction of various metal ions. The reason, we believe, is that both 8 and 8' have very similar, spatially regulated sites in the polymer that are readily able to form stable, metal-ion sandwich complexes, while polymer 9 appears to form a more highly cross-linked, hydrophobic polymer site, with dramatically reduced selectivities and capacities for all metal ions studied (see Table 1).

Our significant new findings in the area of metal-ion-templated polymers can be summarized as follows: 1) we synthesized imprinted polymeric metal-ion sandwich complexes; 2) we could show that thermodynamic stability is a controlling factor for the high selectivity for Cu^{2+} ions in the presence of Zn^{2+} , Ni²⁺, Co²⁺, and Mn²⁺ ions reintroduced to the Zn²⁺-demetalized polymer sites; 3) we found evidence that metal-ion-imprinting is possibly an important parameter for selectivity on reintroduction of divalent metal ions in the absence of Cu²⁺ ions $(Zn^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+})$; and 4) we tentativley postulate that Zn^{2+} -imprinting (the ionic radius of Zn^{2+} and Cu^{2+} being comparable) accounts for the selectivity for Cu²⁺ over Fe³⁺ ions, because the Fe³⁺ ion is usually an ion that can readily compete for any polymer-pendant ligand site due to its favorable charge-to-radius ratio. Future studies will focus on the scope of the metal-ion-templated polymer field with other macrocycles that are hoped to provide high metal-ion selectivities. A continuation of our mono-N-(4-vinylbenzyl) TACN studies with Ag⁺, Hg²⁺, Cd²⁺, and Pb²⁺ ions as templates and subsequent investigations of the templated polymers should refine the understanding of the importance of templating and thermodynamic parameters.

Experimental Section

1: To a stirred solution of TACN (0.50 g, 3.87 mmol) in ethanol (12 mL) was added a solution of LiOH (20 mg, 0.84 mmol) in water (5 mL) in one portion. The resulting cloudy solution was stirred at 50 °C for 2 h and then cooled to ambient temperature. A solution of 4-vinylbenzyl chloride (118 mg, 0.774 mmol) in ethanol (1.0 mL) was added dropwise, and the final reaction mixture was stirred at reflux for 3 h before being stripped in vacuo. The residue was triturated with water (20 mL) and extracted with CH₂Cl₂ (25 mL × 3). The combined organic layer was dried over Na₂SO₄ and stripped in vacuo to give the 1 in about 85% yield (¹H NMR analysis shows 1 to be >90% pure). FAB-MS (*m*-nitrobenzyl alcohol): *m/z* (%): [*M*+H]⁺ 246 (100%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.32 (m, 4H, aromatic H), 6.70 (dd, 1H, vinyl H_a), 5.72 (d, 1H, vinyl H_{b1}), 5.21 (d, 1H, vinyl H_{b2}), 3.69 (s, 2H, benzyl CH₂), 2.71 (m, 12H, TACN CH₂), and 2.43 (s, 2H, NH). Elemental analysis calcd for C₁, sH₂N₃. ²H₂O · 0.25 CH₂Cl₂: C 60.5, H 9.10, N 13.9; found: C 61.2, H 8.84, N 14.1.

2: To a stirred solution of TACN (5.0 g, 38.7 mmol) in anhydrous toluene (88 mL) in a glovebox was added powdered KOH (6.53 g, 116 mmol) slowly, and the resulting suspension was treated with 4-vinylbenzyl chloride (17.7 g, 116 mmol, dropwise). The reaction mixture was heated to 80 °C and stirred at this temperature for 8 h. After it had cooled to room temperature, it was treated with an additional portion of powdered KOH (1.1 g) and stirred for another 10 h. The final reaction mixture was filtered, and the filtrate was stripped in vacuo to give **2** in quantitative yield. FAB-MS (*m*-nitrobenzyl alcohol): m/z (%): $[M + H]^+$ 478 (100%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.31 (m, 4H, aromatic H), 6.69 (dd, 1H, vinyl H₂), 5.74 (d, 1H, vinyl H_{b1}), 5.24 (d, 1H, vinyl H_{b2}), 3.64 (s, 2H, benzyl CH₂), and 2.88 (s, 4H, TACN CH₂). Elemental analysis calcd for C₃₃H₃₉N₃·2 H₂O: C 77.2, H 8.38, N 8.19; found: C 77.6, H 8.09, N 7.99.

3: To a solution of 1 (0.14 g, 0.57 mmol) in MeOH (20 mL) was added a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.16 g, 0.54 mmol) in MeOH (5 mL) in one portion, and the

reaction mixture was stirred at ambient temperature for 48 h and then filtered. The volume of the filtrate was reduced to 6.8 mL to give a solution (ca. 0.085 M) of 3 (this solution was used for the polymerization reactions). The solid 3 was obtained when enough diethyl ether vapor was diffused into this solution. FAB-MS (*m*-nitrobenzyl alcohol): m/z (%): $[M - NO_3^{-1}]^+$ 371 (70%). ¹H NMR (400 MHz, CDCl₃, 25 °C) $\delta = 7.33$ (m, 4H, aromatic Hs), 6.70 (dd, 1H, vinyl H_a), 5.77 (d, 1H, vinyl H_{b1}), 5.28 (d, 1H, vinyl H_{b2}), 4.07 (s, 2H, benzyl CH₂), and 3.22, 2.56 (m, 12 H, TACN CH₂). Elemental analysis calcd for C₁₅H₂₃N₅O₆Zn·CH₃OH: C 41.2, H 5.8, N 15.0, Zn 14.0; found: C 40.1, H 6.1, N 15.4, Zn 13.6.

4: To a vigorously stirred suspension of **2** (0.528 g, 1.11 mmol) in MeOH (50 mL) was added a solution of Zn(NO₃)₂·6 H₂O (0.297 g, 1.00 mmol) in MeOH (5 mL) in one portion, and the reaction mixture was stirred at ambient temperature for 48 h and then filtered. The volume of filtrate was reduced to 15 mL to give a saturated solution (ca. 0.066 M) of **4** (this solution was used for the polymerization reactions). Upon standing, **4** crystallized as off-white needles (80% yield). FAB-MS (*m*-nitrobenzyl alcohol): *m/z* (%): [$M - NO_3^{-1}$ + 603 (3.8%), [$M - NO_3^{-} - HNO_3$]⁺ 540 (7.4%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.32 (m, 4H, aromatic H), 6.69 (dd, 1H, vinyl H₂), 5.76 (d, 1H, vinyl H₂₁), 5.29 (d, 1H, vinyl H₂₂), 4.21 (s, 2H, benzyl CH₂), and 3.17, 2.40 (m, 4H, TACN CH₂). Elemental analysis calcd for C₃₃H₃₉N₅O₆Zn · 4 CH₃OH: C 55.9, H 6.9, N 8.8, Zn 8.2; found: C 55.3, H 5.9, N 8.7, Zn ca. 9.

7: To a solution of 1 (0.18 g, 0.74 mmol) in MeOH (30 mL) was added a solution of Zn(OTf)₂ (0.13 g, 0.37 mmol) in MeOH (10 mL) in one portion, and the reaction mixture was stirred at ambient temperature for 48 h, and then filtered. The volume of filtrate was reduced to 11.0 mL to give a solution (ca. 0.034 M) of 7 (this solution was used for the polymerization reactions). The solid sample of 7 was obtained when the volatiles were removed in vacuo. Electrospray ionization/MS (methanol): m/z (%): $[M - OTf]^+$ 703 (8%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.29 (m, 4H, aromatic H), 6.70 (dd, 1H, vinyl H_a), 5.77 (d, 1H, vinyl H_{b1}), 5.29 (d, 1H, vinyl H_{b2}), 4.07 (s, 2H, benzyl CH₂), and 3.69–2.39 (m, 12 H, TACN CH₂). Elemental analysis calcd for C₃₂H₄₆F₆N₆O₆S₂Zn · 6H₂O: C 39.9, H 6.0, N 8.7, Zn 6.8; found: C 40.0, H 5.4, N 8.8, Zn 6.8.

Typical polymerization procedure with monomer 3: A solution of monomer 3 (0.085M), cross-linking agent DVB (0.066M), and initiator AIBN (0.006M), in MeOH (4 mL) was placed in a 12 mL vial and purged with argon gas for 7 min, after which the vial was capped, heated to $78\,^{\circ}$ C over a 1 h period, and kept at this temperature overnight. The resulting bulk polymer powder (5) was collected on a 0.45 m nylon membrane, washed with hot methanol, dried for analysis, demetalated with 6N HCl to provide 8, which was used for the metal ion selectivity studies (see Table 1). Elemental analysis for 5: C, 61.0; H, 7.22; N, 8.85; Zn, 5.7 (1.33 mmol TACN per gram of resin).

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tion was applied by the program XABS based on F_o and F_c differences. (H. Hope, B. Moezzi, Chemistry Department, University of California, Davis), $\mu = 1.477$ mm⁻¹, max./min. transmission = 0.76/0.61, structure was solved by direct method using SHELXL-93, and refined by a full-matrix least-squares method based on F^2 with 429 parameters, hydrogen atoms were located or added in calculated positions, and refined by using the riding model, R = 0.0339; wR = 0.0944, largest difference peak = 0.480 e Å⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-157. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB21EZ UK (fax: int. code +(1223)336-033; e-mail: depositic chemerys.cam.ac.uk).

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Isolation of a Nonicosahedral Intermediate in the Isomerization of an Icosahedral Metallacarborane**

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The mechanism by which the icosahedral carboranes, their C-substituted derivatives, and their heteroatom analogues rearrange has been the subject of speculation since the 1,2- to 1,7-isomerization of $closo-C_2B_{10}H_{12}$ was reported more than 30 years ago.⁽¹⁾ A number of possible mechanisms have been proposed^[2] on the basis of both experimental observations (product distributions) and theoretical calculations. As far as we are aware, however, the high temperatures generally required for these isomerizations have so far precluded isolation of any intermediate species; the identification of such intermediates is clearly important for judging the relative merits of the various mechanistic proposals.

We have recently shown that targeting molecules that are severely overcrowded can dramatically lower isomerization temperatures in icosahedral metallacarboranes.^[3] We now report the unexpected first isolation and characterization of an intermediate in an icosahedral-to-icosahedral rearrangement. This intermediate, which is closed but not icosahedral in shape, has previously only been identified theoretically.^[21]

Reaction of Na₂[7-Ph-7,8-*nido*-C₂B₉H₁₀] and [(CH₃CN)₂-MoBr(η^3 -C₃H₅)(CO)₂] in THF at 0 °C affords the metallacarborane 1⁻ as a benzyltrimethylammonium (BTMA⁺) salt in good yield. The anion 1⁻ exhibits two bands in the carbonyl region of the IR spectrum at 1924 and 1833 cm⁻¹ (CH₂Cl₂). Crystallographic analysis^[4] confirms that 1⁻ has the expected icosahedral structure with a 3,1,2-MoC₂ heteroatom arrangement (Figure 1).

 $[1-Ph-3,3-(CO)_2-3-(\eta^3-C_3H_5)-3,1,2-closo-MoC_2B_9H_{10}]^-$ 1⁻

 $[Ph_2(CO)_2(\eta^3-C_3H_5)MoC_2B_9H_9]^-$ 2⁻

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Figure 1. Perspective view of I^- . Selected bond lengths [Å] and angles [^a]: C1-C2 1.616(4), C1-C11 1.509(4), Mo3-C1 2.438(3), Mo3-C2 2.418(3), Mo3-C31 1.914(4), Mo3-C32 1.918(4), Mo3-C33 2.335(4), Mo3-C34 2.234(4), Mo3-C35 2.379(3), C31-O31 1.161(4), C32-O32 1.163(4); C31-Mo3-C32 79.4(2).

An analogous product is not obtained from the diphenyl carborane anion. Rather, treatment of $Na_2[7,8-Ph_2-7,8-nido-C_2B_9H_9]$ with the same metal substrate under the same conditions yields 2^- , which shows IR stretching bands at significantly higher frequencies (1954 and 1893 cm⁻¹). A crystallographic study^[5] of the BTMA⁺ salt of 2^- reveals a nonicosahedral *closo* geometry with two 4-connected cluster vertices (occupied by carbon atoms) and two 6-connected vertices (one occupied by Mo, Figure 2). There is only one Mo-C (cluster) connectivity, and it is significant that the two cage carbon atoms are substantially separated.



Figure 2. Perspective view of 2^- . Selected bond lengths [Å] and angles [°]: C1-C11 1.495(10), C2--C21 1.478(10), Mo5-C1 2.260(7), Mo5-C51 1.950(8), Mo5-C52 1.986(9), Mo5-C53 2.395(9), Mo5-C54 2.248(9), Mo5-C55 2.338(9), C51-O51 1.155(9), C52-O52 1.150(9); C51-Mo5-C52 79.4(3).

The ¹H NMR spectrum of 2^{-} in CD₃CN slowly changes at room temperature (over days). This suggests that 2^{-} is a kinetic rather than a thermodynamic product, and identifies it as a potential intermediate in a carbon atom isomerization process. This is confirmed by the quantitative conversion of 2^{-} to 3^{-} upon heating in THF at reflux (30 min); the product Et₄N⁺3⁻ shows carbonyl IR bands (1920 and 1831 cm⁻¹) that are very similar to those of BTMA⁺1⁻. A single crystal X-ray

 $[1,9-Ph_2-3,3-(CO)_2-3-(\eta^3-C_3H_5)-3,1,9-closo-MoC_2B_9H_9]^-$ 3⁻

^[6] H. Irving, R. J. P. Williams, J. Chem. Soc. 1953, 3192.

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