Open-Cage Fullerenes as Ligands for Metals

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Open-Cage Fullerenes as Ligands for Metals

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Abstract

The remarkable structures of open-cage fullerenes with functionalization on the outer surface and an accessible inner void make them interesting ligands for reactions with metal complexes. The behaviors of open-cage fullerenes in reactions with various metal complexes are examined and compared to corresponding reactions with intact fullerenes. Structural results from X-ray diffraction are emphasized. Open-cage fullerenes frequently undergo unanticipated structural changes such as carbon-carbon bond cleavage upon reactions with metal complexes. Much more remains to be learned about the possibility of inserting metal ions larger than Li^+ into the interior void of these open-cage fullerenes and about the effects of redox reactions on metal complexes of open-cage fullerenes.

Introduction.

After the discovery that C_{60} could be obtained in macroscopic amounts,[1]chemists seized on the opportunity to chemically modify the readily accessable outer surface of this highly symmetrical molecule.[2] One approach involved the creation of openings in the fullerene cage that could allow small molecules and atoms to enter the interior void to produce endohedral fullerenes.[3,4] Eventually, a wide array of open-cage fullerenes were prepared, and their abilities to host guest molecules in their interior was explored. [5,6,7,] The use of the "molecular surgery" approach allowed endohedral fullerenes such as $H_2@C_{60}$ and $H_2O@C_{60}$ to be synthesized by chemically preparing an open-cage fullerene, inserting the small molecule and then chemically closing the opening.[8,9] . Other species that have been introduced into the interior of open-cage fullerenes include: NH_3, H_2O_2, CH_4, and the rare gasses.[7]

Fig. 1 shows drawings of a representative example of an open-cage fullerene, **MMK-15**, as determined by single crystal X-ray diffraction.[10] (We use the authors' initials followed by the number used in the original article to designate this and other open-cage molecules discussed here.) The picture on the left shows a conventional thermal ellipsoid drawing of the molecule with the carbons atoms of the 13-membered orifice colored dark blue and the two keto groups with the red oxygen atoms on opposite sides of the rim. An imine nitrogen atom and a sulfur atom are part of the cage opening. The picture on the right shows a space-filling drawing of the same molecule from a perspective that looks through the opening into the cage. The sliver of grey at the center between the two red oxygen atoms is the orifice that allows us to see the opposite side of the cage interior. While small, this opening is large enough to allow dihydrogen to enter the fullerene cavity to produce the endohedral **H_2@MMK-15**.[9]

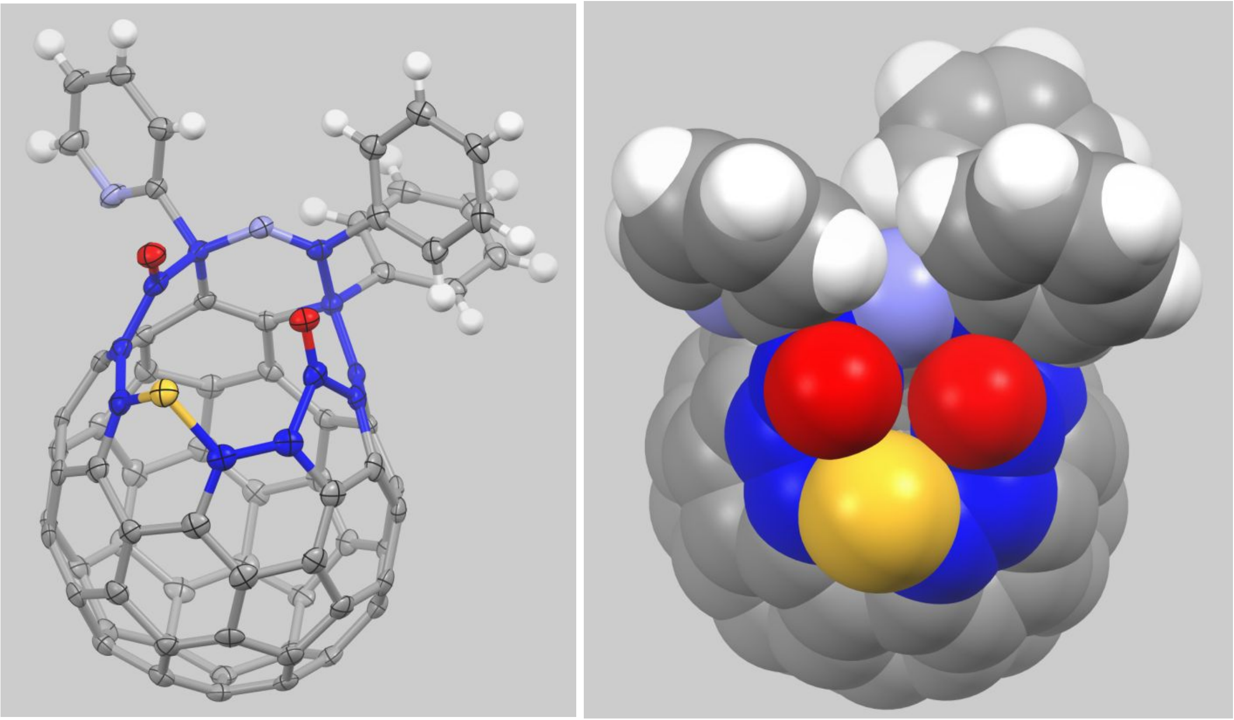


Fig. 1 Drawings of a representative open-cage fullerene, **MMK-15**. Left, a drawing using thermal ellipsoids. Right, a space-filling drawing from a perspective that looks down on the opening into the cage. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; hydrogen, white; nitrogen, pale blue; oxygen, red; sulfur, yellow. From data in Y. Murata, M. Murata and K. Komatsu, *Chem. Eur. J.*, 2003, **9**, 1600-1609.

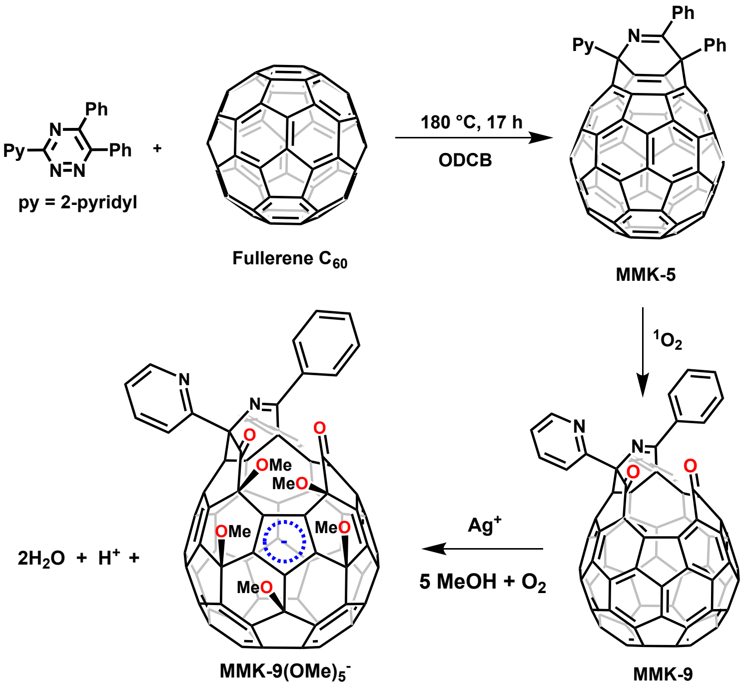
In addition to hosting rare gasses and small molecules, endohedral fullerenes can contain one to four metal atoms, sometimes along with main group atoms that form clusters.[11,12,13] In general, endohedral metallofullerenes are obtained in low yield by a gas phase process that involves electric arc vaporization of graphite rods doped with the appropriate metal oxide. However, until very recently, metal ions have not been found to enter the interior of open-cage fullerene (*vide infra*). Nevertheless, the ability to insert metal atoms or ions into open-cage fullerenes could provide means to obtain such guest/host molecules in higher yield that the current gas phase processes. If endohedral metallofullerenes became available in greater quantities, then some of their potential uses (gadolinium enodhedrals as magnetic resonance imaging (MRI) relaxation agents, [14,15,16] lutetium endohedrals as X-ray contrast agents and radiodiagnostics,[17,18] *etc.*) might be realized.

In this perspective, the use of open-cage fullerenes as ligands will be reviewed. There are several properties of open-cage fullerenes that make them interesting ligands. The cage architecture itself provides an unusual and attractive framework for coordination. Moreover, open-cage fullerenes retain some of the electrochemical behavior that is observed with intact fullerenes and can be used to introduce redox functionality into their metal complexes[19,20,21] Additionally, open-cage fullerenes are chromophores with abosrption extending in the visible and near IR regions. The cage opening reactions can also add Lewis basic functional groups around the orifice that may be used to bind metal centers. This article will examine the coordination of metal centers to open-cage fiullerenes and will compare that bonding to the bonding of the same metal centers to C_{60}. The coordination of metal complexes to pristine C_{60} and other fullerenes has been reviewed.[22,23,] In general, η^2-bonding to the 6:6 ring junctions of C_{60} is the dominant means of attachment of single metal centers to C_{60},[24,25] although cases of η^1-bonding are known.[26] Metal clusters are also known to bind to C_{60} in a variety of fashions.[27] A related topic, the behavior of functionalized, but intact, fullerenes as ligands has also been reviewed.[28]

A major focus of this article concerns the structures of complexes of open-cage fullerenes with metal centers as determined by single crystal X-ray diffraction, since this technique offers the best means to understand the three dimensional nature of these complex molecules. A nice review of a related topic, the coordination of metal complexes to buckybowls, polycyclic hydrocarbon molecules that map onto the surface of C_{60} such as corannulene, is available,[29] as is a review on metal ion coordination to reduced buckybowls and related hydrocarbon anions.[30] In general, these buckybowls have a modest curvature that produces an interior that is considerably more open than the interior cavities of open-cage fullerenes discussed here.

The unexpected reactivity of the open-cage fullerene, MMK-9.

The open-cage fullerene, **MMK-9**, is readily available from C_{60} by the two-step synthetic route shown in Scheme 1.[10] The structure of **MMK-9** as determined by single crystal X-ray diffraction is shown in Fig. 2. **MMK-9** possesses a 12-membered-ring orifice which is highlighted in blue in Fig. 2. The opening in this cage appears to be too small to allow small molecules to enter the interior of the molecule.[31]



Scheme 1 The formation of **MMK-9** and its reaction with methanol in the presence of Ag^+ and dioxygen.

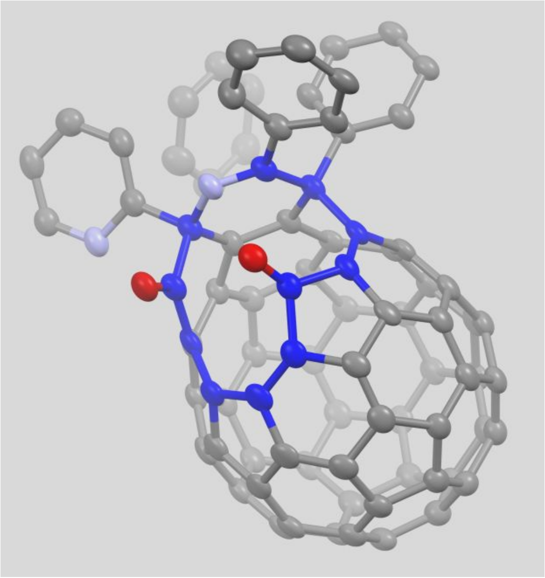
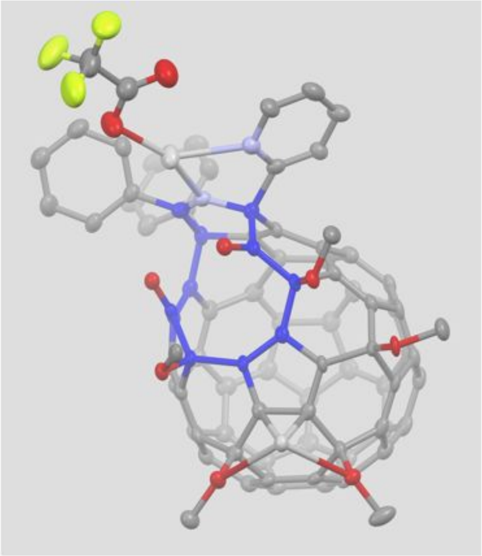


Fig. 2 The structure of the open-cage fullerene **MMK-9**. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; nitrogen, pale blue; oxygen, red. From data in A. Aghabali, S. Jun, M. M. Olmstead, and A. L. Balch, *J. Am. Chem. Soc.*, 2016, **138,** 16459-16465.

Reactions with silver(I) salts. Allowing a methanol solution of silver trifluoroacetate to diffuse into a dichloromethane solution of **MMK-9** open to the atmosphere produced black crystals of **{MMK-9(OCH$_3$)$_5$Ag(AgO$_2$CCF$_3$)}$_2$•4CH$_2$Cl$_2$**.[32] There are several interesting features of this compound. Remarkably, five CH$_3$O groups have been added to the open-cage fullerene at the ends of the five double bonds that radiate from a pentagon just below the cage opening (seen in Fig. 3) to yield a mono-anionic open-cage fullerene. This pattern of addition of OMe groups is similar to the addition pattern of phenyl or methyl groups observed in the preparation of (η^5-C$_{60}$Ph$_5$)Tl and the ferrocene/[C$_{60}$]fullerene hybrid, (η^5-C$_{60}$Me$_5$)Fe(η^5C$_5$H$_5$), both of which begin with the reaction of Me$_2$SCuBr and RMgBr (R = Ph or Me) with C$_{60}$.[33,34] In contrast to the air-sensitive syntheses like those just mentioned, the reaction that produces **{MMK-9(OCH$_3$)$_5$Ag(AgO$_2$CCF$_3$)}$_2$•4CH$_2$Cl$_2$** requires exposure to air. It appears that dioxygen is the oxidant that added the five CH$_3$O groups to the open-cage fullerene. If the reaction is conducted under an inert atmosphere, no crystals form. There is no evidence that silver is reduced in the process. The addition of five CH_3O groups is a unique reaction that occurs with **MMK-9**. Under comparable conditions, C_{60} does not react in this fashion. However, in ethanol solution in air, silver(I) nitrate does react with C_{60} to produce black crystals of $C_{60}\{Ag(NO_3)\}_5$ in which a network of silver nitrate ions surrounds each fullerene.[35]



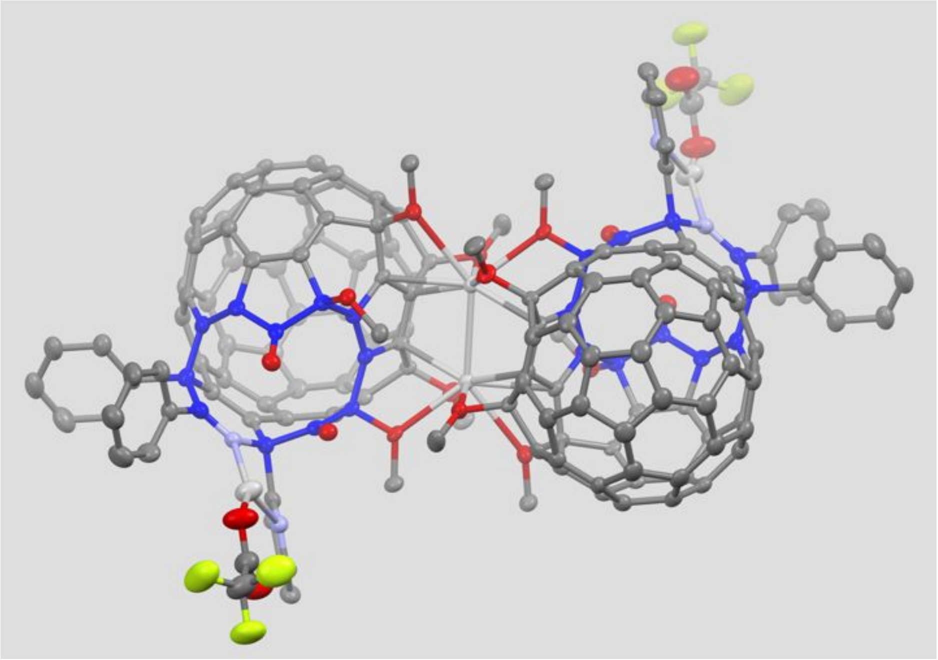


Fig. 3 The structure of **{MMK-9-(OCH$_3$)$_5$Ag(AgO$_2$CCF$_3$)}$_2$** with hydrogen atoms removed for clarity. Top, the asymmetric unit. Bottom, the complete centrosymmetric dimer. Color scheme: carbon, grey except for those atoms on the rim of the opening which are dark blue; nitrogen, pale blue; oxygen, red; silver, white; fluorine, yellow. From data in A. Aghabali, S. Jun, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc*., 2016, **138,** 16459-16465.

The bonding of silver ions to the open-cages is another interesting feature of this molecule. There are two silver ions in the asymmetric unit. One is at the periphery of the molecule and chelated by the two nitrogen atoms to form a five-membered ring and by an oxygen atom of the trifluoroacetate ion. The other silver ion (Ag1) is coordinated by two methoxy groups and is η^2-coordinated to two carbon atoms at a 5:6 ring junction on the open-cage fullerene. In the centrosymmetric dimer, Ag1 is also bonded to its symmetry generated counterpart, Ag1', with an Ag1−Ag1′ distance of 2.8368(12) Å. Such a short Ag1−Ag1′ distance indicates that there is an argentophilic interaction at the center of the dimer.[36] Additionally, each of the two central silver ions forms an η^1-bond to a fullerene cage in the adjoining open-cage. Thus, each of the central silver ions interacts with the adjacent silver ion, four methoxy groups (two from each open-cage), two carbon atoms from one open-cage and one carbon atom on the other open-cage.

Black crystals containing polymeric **$[\{\mathrm{MMK\text{-}9(OCH_3)_5Ag(AgOCH_3)}\}_2\cdot\mathrm{H_2O}]_n$** formed when a dichloromethane solution of MMK-9 was slowly diffused to a methanol solution of silver nitrate again with exposure to air. These crystals contain the same modification of **MMK-9** in which five CH_3O units are added to each open-cage fullerene and similar dimerization of two open-cages about a pair of closely connected silver ions (Ag···Ag distances, 2.853(1), 2.863(1) Å) as seen in Fig 3. To complicate matters, there are two open-cage fullerenes in the asymmetric unit, but both have similar structures and both pack about centers of symmetry. Polymerization occurs due to coordination of a silver ion that is chelated by the two nitrogen atoms of one open –cage to a pair of carbon atoms at a 6:6 ring junction on the periphery of an adjacent open-cage. This arrangement can be seen at the top and bottom of Fig. 4. Charge balance is achieved by the presence of a loosely bound methoxide ion that is near the silver ions chelated by two nitrogen atoms. Neither **$\{\mathrm{MMK\text{-}9(OCH_3)_5Ag(AgO_2CCF_3)}\}_2\text{•}4\mathrm{CH_2Cl_2}$** nor **[{MMK-**

9(OCH$_3$)$_5$Ag(AgOCH$_3$)}$_2$·H$_2$O]$_n$ is soluble in organic solvents or water. Consequently, the solution properties of these compounds could not be studied.

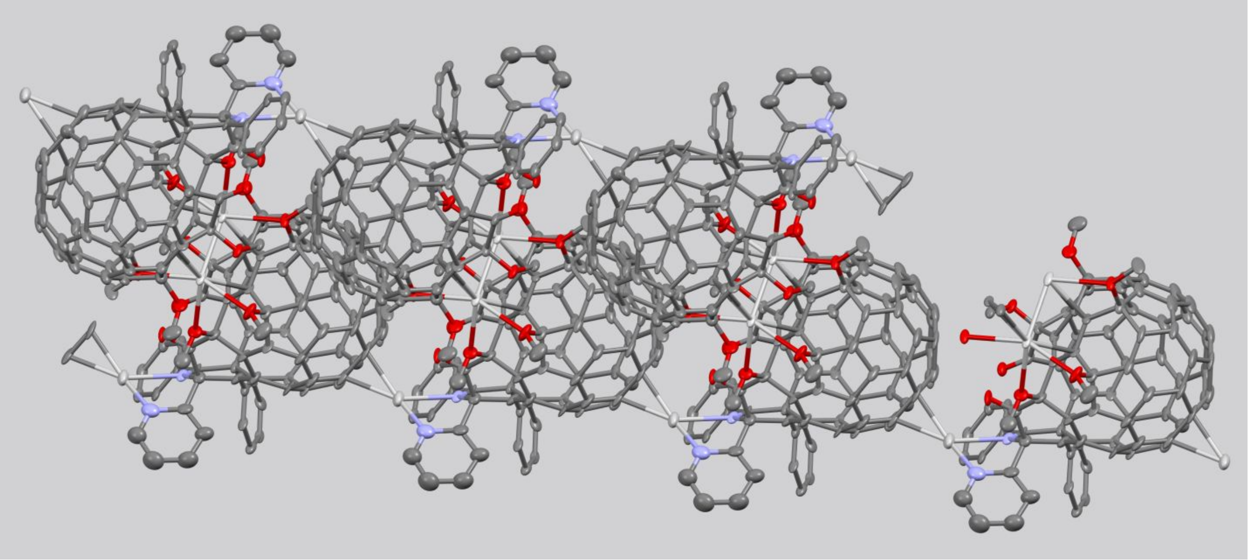
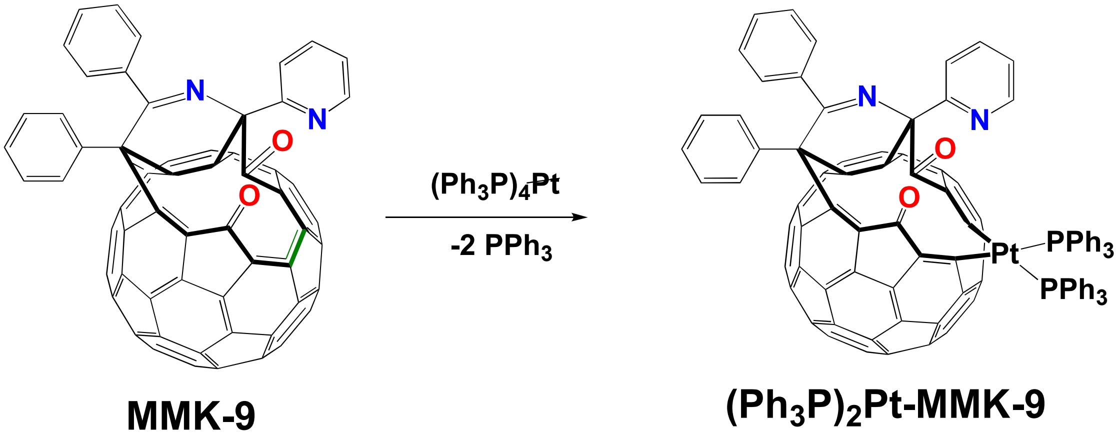


Fig. 4 The structure of one of the two polymeric chains in **[{MMK-9(OCH$_3$)$_5$Ag(AgOCH$_3$)}$_2$•H$_2$O]$_n$**. Color scheme: carbon, grey; nitrogen, pale blue; oxygen, red; silver, white. Hydrogen atoms, the loosely bound methoxide ions near the silver ions chelated by two nitrogen atoms, and the solvate water molecules are omtiied for clarity. From data in A. Aghabali, S. Jun, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc*., 2016, **138,** 16459-16465.

Reaction with (Ph$_3$P)$_4$Pt. Addition of (Ph$_3$P)$_4$Pt to MMK-9 in dioxygen-free toluene produced the adduct **(Ph$_3$P)$_2$Pt-MMK-9** in 46 % yield after 90 minutes of stirring at room temperature.[37] The structure of the adduct is shown in Fig 5. Remarkably, a platinum atom has inserted itself into a C-C bond of the open-cage fullerene to become part of the fabric of the fullerene cage. In **(Ph$_3$P)$_2$Pt-MMK-9** the distance between the two carbon atoms coordinated to platinum is 2.59(1) Å, whereas the corresponding C-C bond length in **MMK-9** is 1.533(5) Å. For comparison, in $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ the Pt-C bond lengths are 2.145(24) and 2.115(23) and the C-C bond length is 1.502(30) Å.[22]



Scheme 2 The reaction of **MMK-9** with $(Ph_3P)_4Pt$.

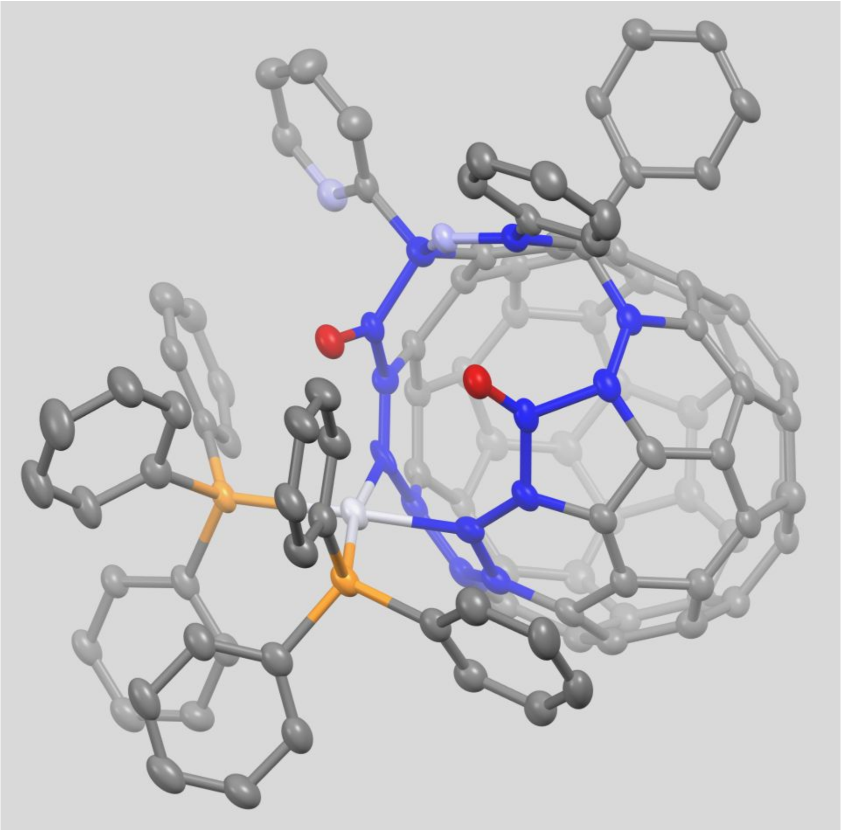
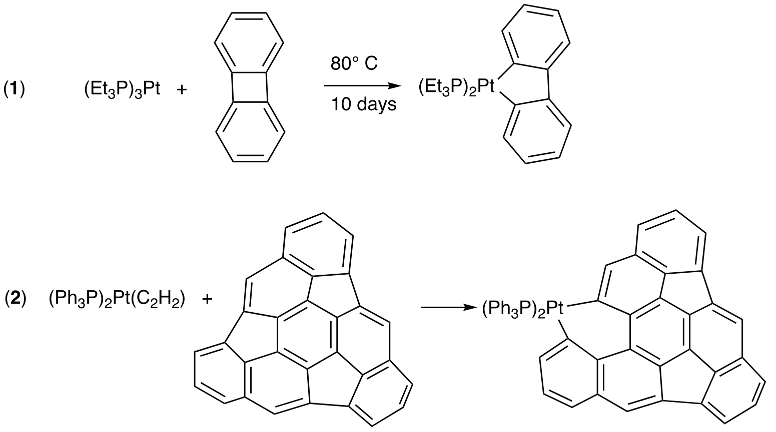


Fig. 5 The structure of **(Ph$_3$P)$_2$Pt-MMK-9**. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; nitrogen, pale blue; oxygen, red; platinum white; phosphorus, orange. From data in S. R. Gralinski, M. Roy, L. M. Baldauf, M. M. Olmstead and A. L. Balch, *Chem. Commun*., 2016, **138,** 16459-16465.

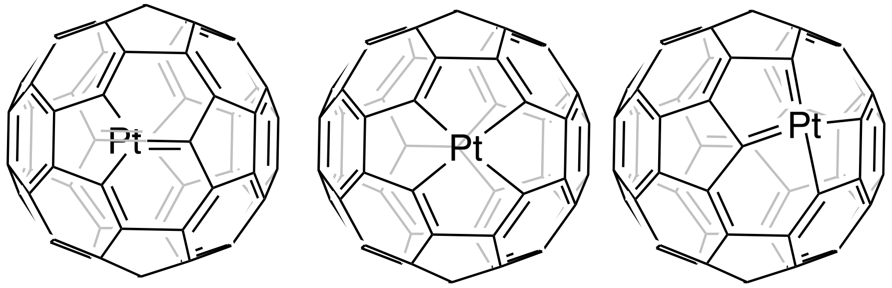
(Ph$_3$P)$_2$Pt-MMK-9 is soluble in toluene, carbon disulfide, and *o*-dichlorobenzene. It is quite stable at room temperature and survives chromatography on silica gel. Cyclic voltammetry in *o*-dichlorobenzene reveals that **(Ph$_3$P)$_2$Pt-MMK-9** undergoes a one-electron reduction at a potential considerablly more negative than that of **MMK-9** itself.

Two other related oxidative addition reactions involving C-C bond breaking and oxidative addition to Pt(0) are outlined in Scheme 2. Both require higher tempertures and longer reaction times than needed for the addition of $(Ph_3P)_4Pt$ to **MMK-9**. As seen in reaction (**1**) in Scheme 2, biphenylene reacts with $(Et_3P)_3Pt$ at 80 C° for 10 days to produce the C-C bond cleavage product.[38] As shown in reaction (**2**) in Scheme 2, semibuckminsterfullerene ($C_{30}H_{12}$) requires 15 hr reaction in toluene followed by one hour of heating under reflux with $(Ph_3P)_2Pt(C_2H_4)$ to produce only a 5-10 % yield of the C-C bond cleavage product.[39]



Scheme 3 Examples of carbon-carbon bond cleavage by oxidative addition of $(R_3P)_2Pt^0$.

The formation of **$(Ph_3P)_2$Pt-MMK-9** offers a suggestion that heterofullerenes containing platinum may be eventually synthesized through solution chemical means, since **$(Ph_3P)_2$Pt-MMK-9** has a platinum atom as an intergral part of the cage itself. The heterofullerenes, $C_{59}Pt$ and $C_{58}Pt$ shown in Scheme 4, in which a platinum atom replaces one or two carbon atoms in C_{60}, have been detected in mass spectrometric studies of the laser ablation of electrochemically deposited films of C_{60} and platinum.[40,41] Their structures have been examined through computational studies.[40,41]

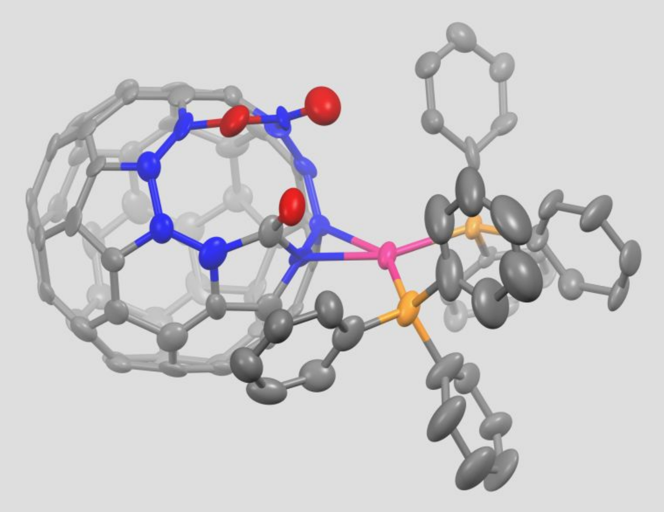


$C_{59}Pt$ $C_{58}Pt$ 6:6 isomer $C_{58}Pt$ 6:5 isomer

Scheme 4 Platinium containing heterofullerenes.

Conventional η^2-bonding of $(Ph_3P)_2Pt$ and $(Ph_3P)_2Pd$ units to the rims of open-cage fullerenes.

Several open-cage fullerenes have been found to form adducts with $(Ph_3P)_2Pt$ and $(Ph_3P)_2Pd$ units. Fig. 6 shows the structures of two adducts involving coordination of $(Ph_3P)_2Pd$ groups onto two different open-cage fullerenes. [42] In **ZZYSJG-4** a single $(Ph_3P)_2Pd$ group has bonded to a C-C double bond on the rim of the 11-membered orifice of the cage.[42] Otherwise, the open-cage is unaltered. In **ZZYSJG-5a** two $(Ph_3P)_2Pd$ groups have been added to C-C double bonds on the rim of a 13-membered ring of different open-cage fullerene, again without any other alteration of the open-cage.[42] **ZZYSJG-4** and **ZZYSJG-5a** are remarkably stable in solution**.** Their synthesis from either $(Ph_3P)_4Pd$ or $Pd(O_2CCH_3)_2$ and Ph_3P was conducted under ambient conditions, and the complexes survived chromatographic purification.



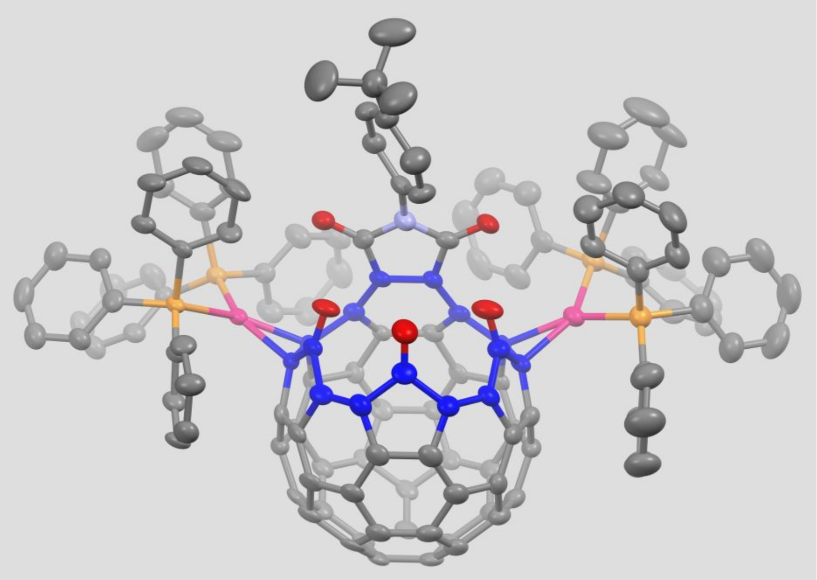


Fig. 6 Top, the structure of the palladium complexes **ZZYSJG-4**. Bottom. The structure of **ZZYSJG-5a**. Hydrogen atoms have been removed for clarity. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; oxygen, red; palladium, pink; phosphorus, orange. From data in H. Zhang, Z. Zhou, L. Yang, J. Su, P. Jin and L. Gan, *Organometallics,* 2019, **38**, 3139−3143.

Reaction of $(Ph_3P)_4Pt$ with an open-cage fullerene bearing a 19-membered orifice followed by reaction of the resulting $Pt(PPh_3)_2$ adduct with 1,2-diaminobenzene produced **LGG-η^2-[OCF-**

2]Pt(PPh$_3$)$_2$, whose structure is shown in Fig. 7.[43] Interestingly, a water molecule was drawn into the interior void of the open-cage during the synthesis of this molecule. As was true for the palladium complexes described above, **LGG-*η*^{2}-[OCF-2]Pt(PPh$_3$)$_2$** was prepared under ambient conditions and is stable to air and chromatography. The platinum atom is *η*^{2}-coordinated to a double bond on the rim of the open-cage fullerene. The C-C bond distance at the coordination site is 1.530(8) Å

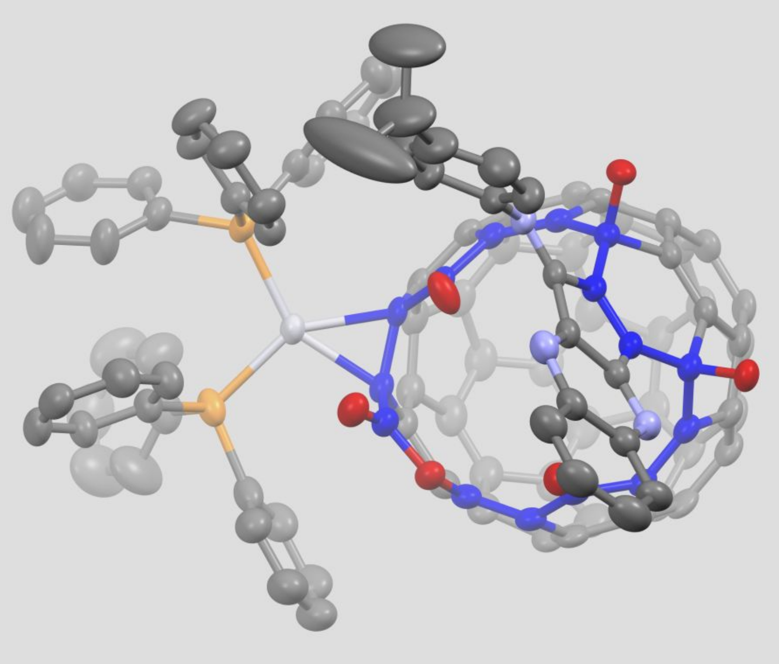


Fig. 7 The structure of the platinum complex **LGG-*η*^{2}-[OCF-2]Pt(PPh$_3$)$_2$** with hydrogen atoms and the water molecule inside the cavity removed for clarity. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; nitrogen, pale blue; oxygen, red; platinum, white; phosphorus, orange. From data in Z. Liu, R. Gao, L. Gan, Synthesis of *η*^{2}-platinum complexes on the rim of open-cage fullerene. *J. Organomet. Chem*. 2023, **1001**, 122880.

Gan and co-workers have prepared an open-cage fullerene with a 17-membered orifice that has three keto groups, a carboxylate and one ester carbonyl group protruding from the orifice and available for metal binding.[44] This open-cage fullerene reacts with $Rh_2(CO)_4Cl_2$ to form several rhodium complexes that have not been obtained in crystalline form and with $(Ph_3P)_4Pt$ to form **GLLSG-3**, whose structure is shown in Fig 8. The structure of **GLLSG-3** involves both η^2-bonding of an $(Ph_3P)_2Pt$ unit to two carbon atoms on the rim of the cage opening as well as coordination of a sodium ion to oxygen atoms that are arrayed along the cage opening. Additionally, a water molecule is enclosed within this open-cage fullerene. The top of Fig. 8 shows the asymmetric unit with the sodium ion coordinated by two of the keto groups on the orifice as well as by the carboxylate. The bottom of Fig. 8 shows the dimeric structure, which is formed by packing of two of the open-cages about a crystallographic center of symmetry. Each sodium ion acts as a bridge between the two cages and is coordinated by three oxygen atoms from one cage and by two oxygen atoms from the adjacent cage, as shown in the top part of the figure.

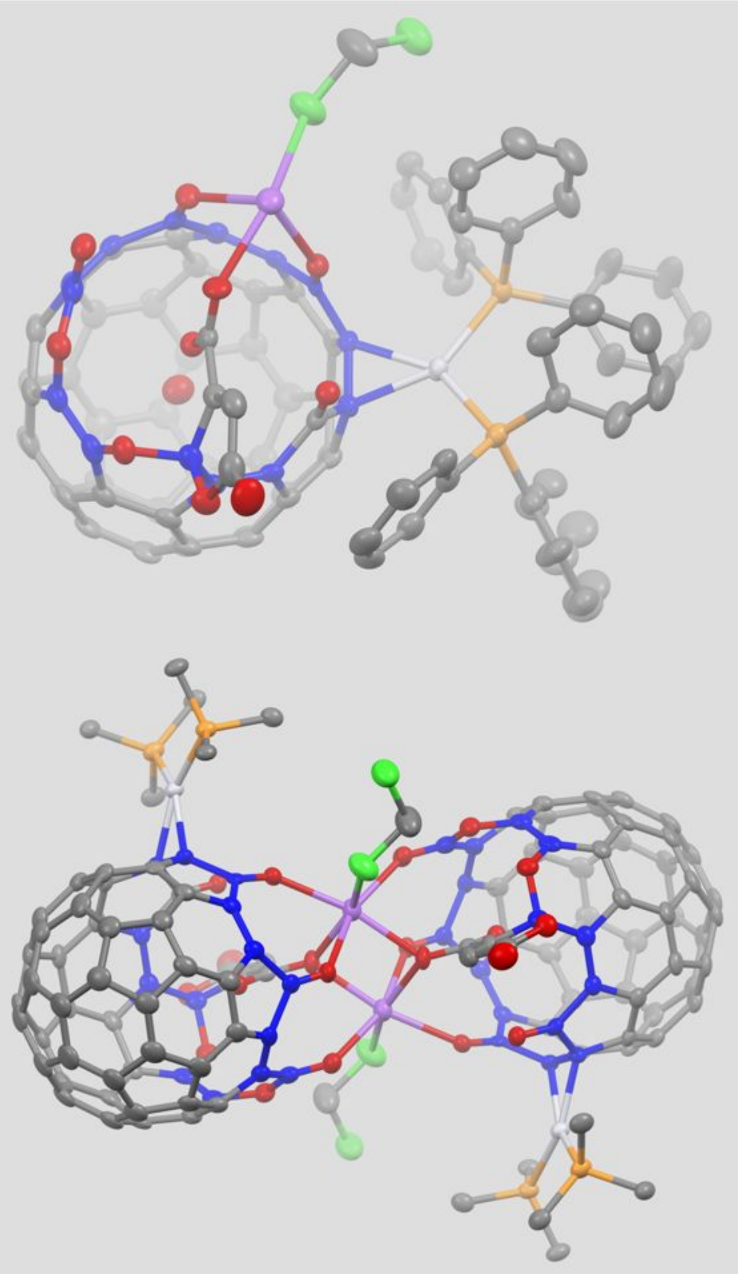
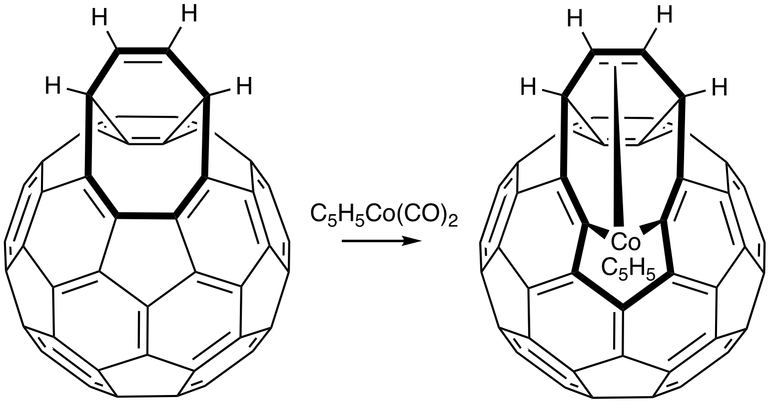


Fig. 8 The structure of **GLLSG-3** with hydrogen atoms removed for clarity. Top, the asymmetric unit. Bottom, the centrosymmetric dimer with only the ipso carbon atoms of the triphenylphosphine ligands shown and the interior water molecule removed for clarity. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; oxygen, red; platinum white; phosphorus, orange; chlorine, green. From data in R. Gao, Z. Liu, Z. Liu, J. Su and L. Gan, *J. Am. Chem. Soc.* 2023, **145**, 18022−18028.

Metal atom coordination and orifice expansion with the bisfulleroid, $C_{64}H_4$.

Rubin and coworkers prepared the bisfulleroid $C_{64}H_4$ (**AVAKR-3**, see Scheme 5), which contains an eight-membered opening into the fullerene cage.[45] Reaction of **AVAKR-3** with (η^5-C_5H_5)Co(CO)$_2$ resulted in insertion of the colablt atom into a C-C bond of the bisfulleriod to produce **AVAKR-1**, as shown in Scheme 5. The structure of **AVAKR-1** is shown in Fig. 9. The cobalt atom is bonded to two carbon atoms of the cage in η^1-fashion and to the olefinic bond of the added C_4H_4 unit in η^2-fashion. The separation between the two carbon atoms of the cage that are connected to cobalt is 2.41(1) Å. The C-Co bond lengths to these cage carbon atoms are 1.902(8) and 1.923(8) Å. Unfortunately, the reaction conditions used to make **AVAKR-1** were not reported. For comparison, (η^5-C_5H_5)Co(CO)$_2$ reacts with C_{60} to form the remarkably stable (η^5-C_5H_5)Co(CO)(η^2-C_{60}), in which the double bond of the fullerene at a 6:6 ring junction replaces one of the carbonyl ligands on cobalt.[46]



AVAKR-3
$C_{64}H_4$

AVAKR-1

Scheme 5 Addition of (η^5-C_5H_5)Co(CO)$_2$ to the bisfulleroid, $C_{64}H_4$

The reaction of **AVAKR-3** with $Os_3(CO)_{10}(NCMe)_2$ in refluxing chlorobenzene solution produces **LY-3**, whose structure is shown in Fig. 9.[47] As with the reaction with (η^5-C_5H_5)Co(CO)$_2$, a metal atom is inserted into a carbon-carbon bond of the bis-fulleroid. In **LY-3**, the osmium atom is coordinated to the open-cage fullerene through two σ Os-C bonds to carbon atoms formerly part of a pentagonal ring and π coordination to the double bond in the added C_2H_4 unit. The coordination of the osmium atom is completed by three terminal carbon monoxide ligands. For comparison, the reaction of $Os_3(CO)_{10}(NCMe)_2$ with pristine C_{60} yields $Os_3(CO)_{10}(NCCH_3)(\eta^2\text{-}C_{60})$.[48]

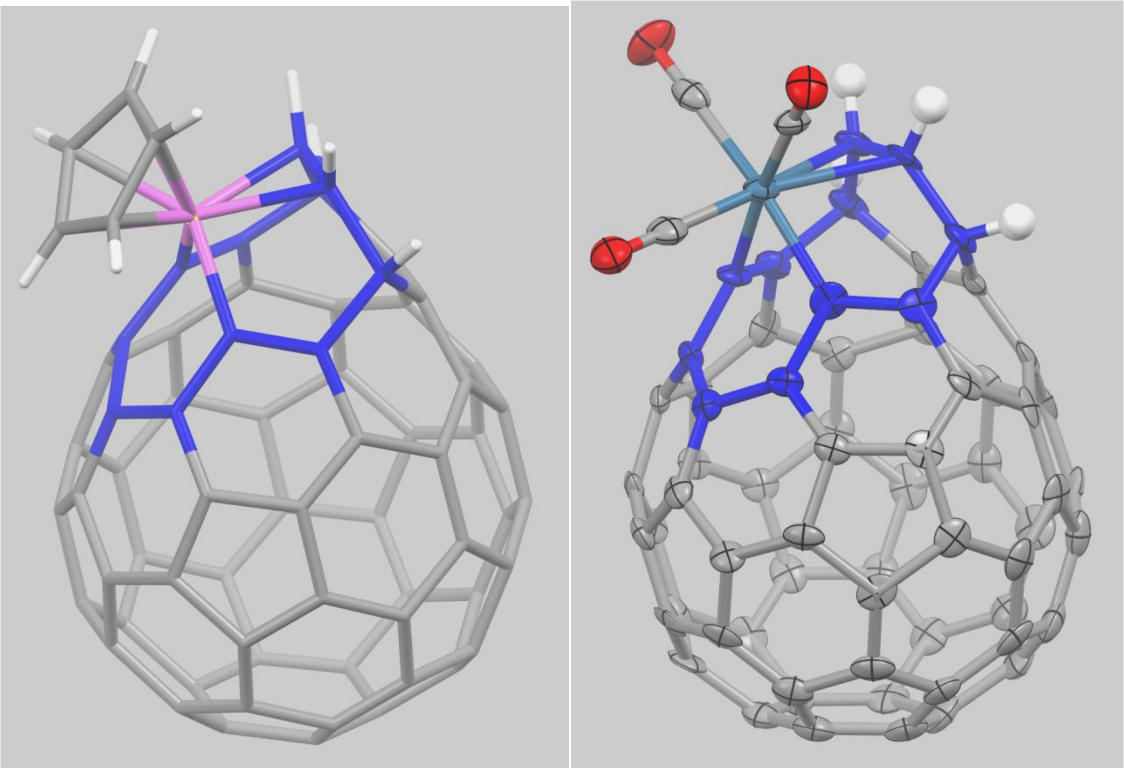
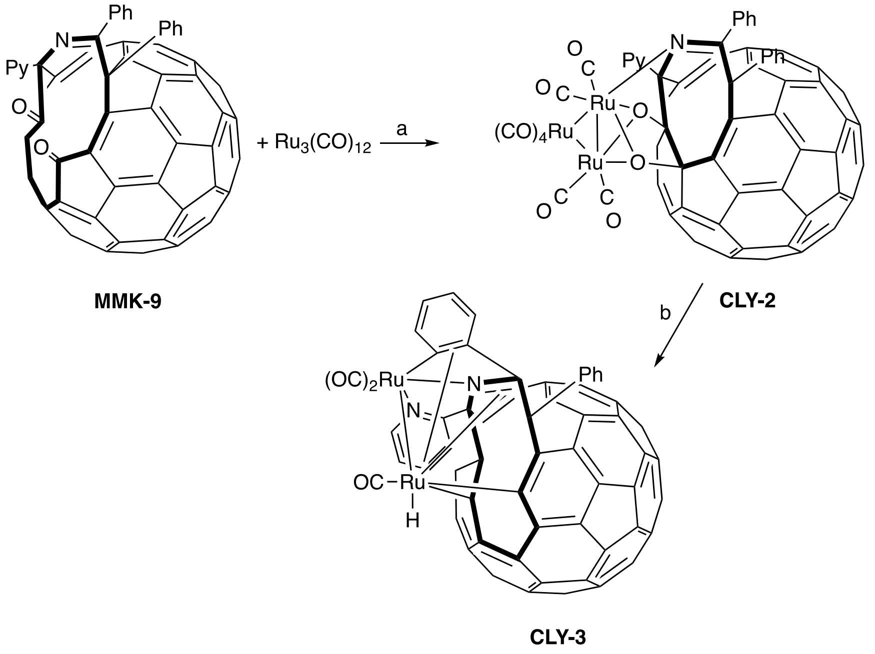


Fig. 9 Left, the structure of **AVAKR-1**. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; cobalt, pink, hydrogen, white. From data in M.-J. Arce, A. L. Viado, Y.-Z. An, S.I. Khan, Y. Rubin, *J. Am. Chem. Soc.* 1996, **118**, 3775-3776. Right, the structure of **LY-3.** Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; osmium, teal, hydrogen, white. From data in S.-T. Lien and W.-Y. Yeh, *J. Organomet. Chem*. 2012, **715**, 69-72.

Further reations of MMK-9: changes in orifice size caused by reactions of $Ru_3(CO)_{12}$ with two open-cage fullerene isomers.

The open-cage fullerene, **MMK-9**, has a 12-membered ring opening as shown in Scheme 5. **MMK-9** reacts with $Ru_3(CO)_{12}$ to produce **CLY-2**, whose structure is shown in Fig 10.[49] In the process, the orifice size has been reduced from a 12-membered ring to a 8-membered ring and a new carbon-carbon bond has been formed between the two ketone carbon atoms in **MMK-9.** However, the bond length of this new C-C bond is rather long, 1.675 Å, when compared to a normal C-C single bond distance of 1.54 Å.



Scheme 6 Products of the reactions of the open-cage fullerene **MMK-9** with $Ru_3(CO)_{12}$. Conditions: a, boiling in chlorobenzene for 30 min; b, pyrolysis under vacuum for 30 min.

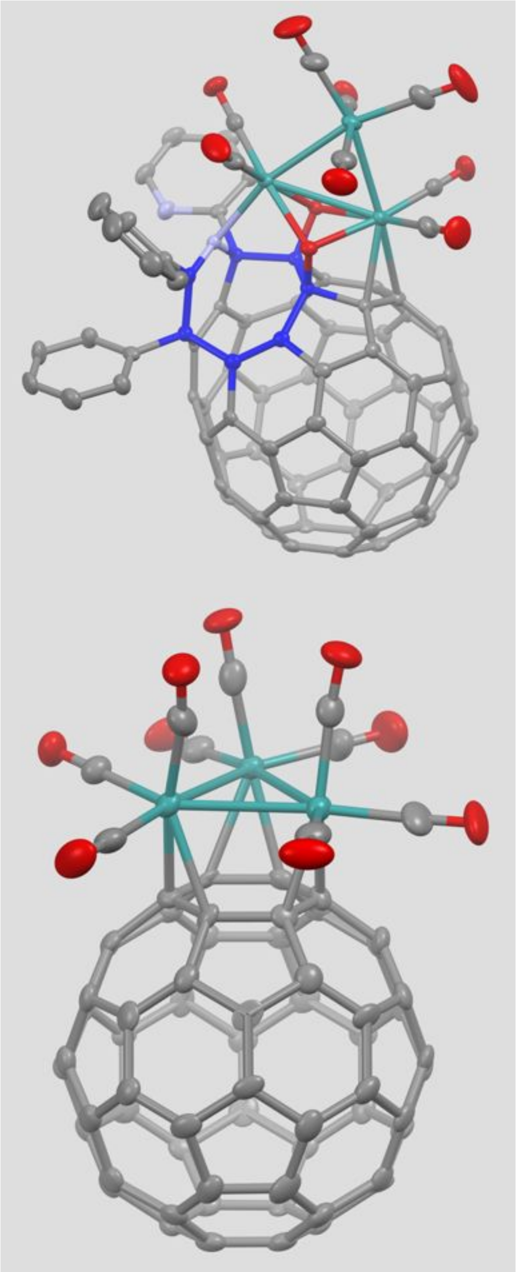


Fig. 10 Top, the structure of the ruthenium complex **CLY-2** with hydrogen atoms removed. Color scheme: carbon, grey except for those on the rim of the opening, which are dark blue; oxygen, red; ruthenium, green. From data in C.-S. Chen, Y.-F. Lin and W.-Y. Yeh, *Chem. Eur. J.* 2014, **20**, 936 – 940. Bottom: the structure of $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ from data in H.-F. Hsu and J. R. Shapley, *J. Am. Chem. Soc.* 1996, **118**, 9192-9193.

In **CLY2** only two of the three ruthenium atoms from $Ru_3(CO)_{12}$ interact with the open-cage fullerene. One of these two ruthenium atoms is coordinated to the two oxygen atoms of the open-cage fullerene and to a C-C double bond that is not on the rim of the orifice. The other ruthenium atom is coordinated to the two oxygen atoms of the open-cage fullerene, and to the imine nitrogen atom of the cage. In contrast, in $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$, which is the product of the reaction between $Ru_3(CO)_{12}$ and C_{60}, all three ruthenium atoms are coordinated to three C-C double bonds of the fullerene to produce a much simpler structure.[50]

Pyrolysis of **CLY2** under vacuum produces **CLY3** as shown in Scheme 5**.** In the process, the eight-membered opening in **CLY2** is expanded to a ten-membered opening in **CLY3**, and an $Ru(CO)_4$ unit is lost. The structure of **CLY3** is shown in Fig. 11. The boding of the ruthenium atoms to this open-cage fullerene is complicated. One ruthenium atom is connected to two carbon atoms on opposite sides of the orifice, to the C-N double bond, and in η^2-fashion to two carbon atoms of one of the phenyl rings attached to the cage, while the other ruthenium atom is bonded to the imine nitrogen atom, the pyridyl nitrogen atom, and to one of the phenyl groups of the cage in η^1-fashion.

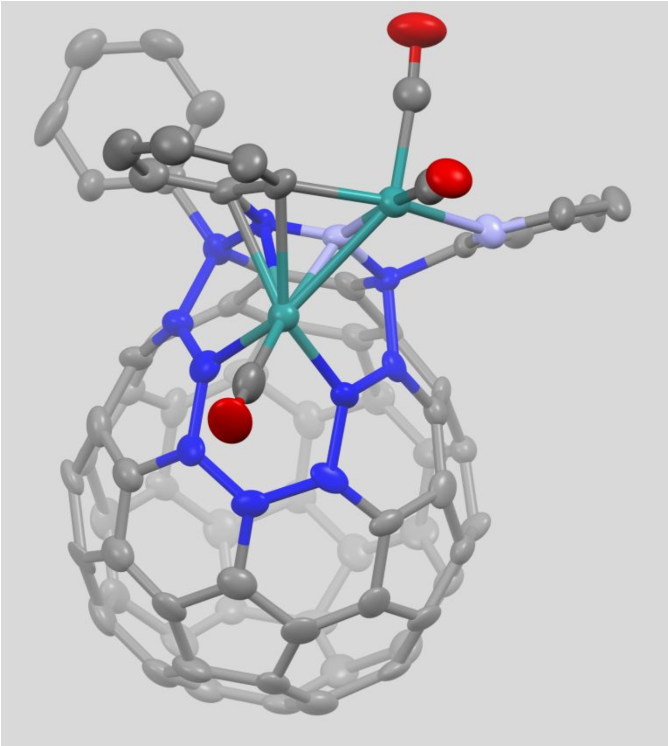
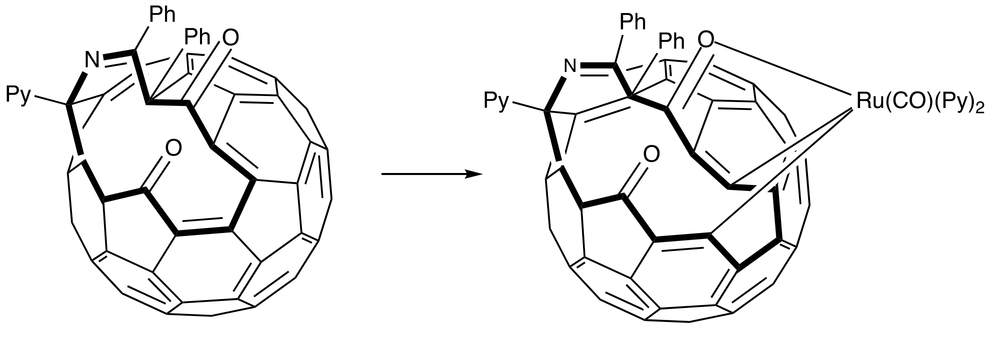


Fig. 11 The structure of the ruthenium complex **CLY-3** with hydrogen atoms removed. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; oxygen, red; ruthenium, green. From data in C.-S. Chen, Y.-F. Lin and W.-Y. Yeh, *Chem. Eur. J.* 2014, **20**, 936 – 940.

The reaction of **CLY-1b**, which is an isomer of **MMK-9**, with $Ru_3(CO)_{12}$ followed a different course, one that involves ring expansion rather than ring contraction as shown in Scheme 7. The product of this reaction was **CLY-4** with a 15-membered ring opening, whose structure is shown in Fig. 12. In this product, a single ruthenium atom is connected to the cage through two carbon atoms on either side of the orifice and through an oxygen atom of one of the keto groups.



CLY-1b **CLY-4**

Scheme 7. Products of the reactions of the open-cage fullerene **CLY-1b** with $Ru_3(CO)_{12}$. Conditions: boiling in chlorobenzene folowed by treatment with pyridine.

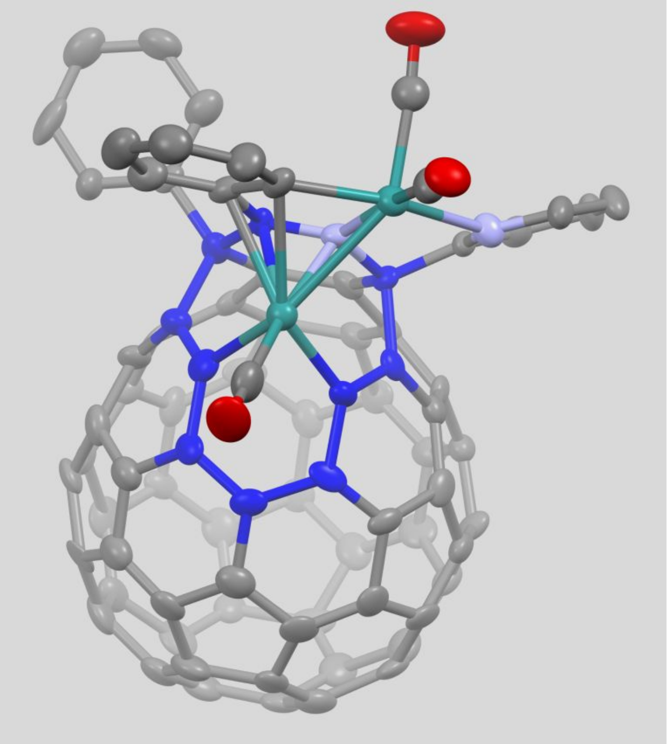
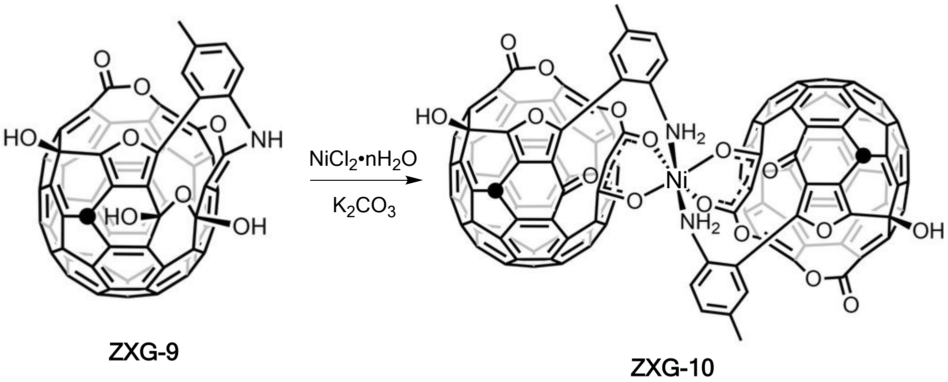


Fig. 12 The structure of the ruthenium complex **CLY-4** with hydrogen atoms removed. Color scheme: carbon, grey except for those on the rim of the opening which are dark blue; oxygen, red; ruthenium, green. From data in C.-S. Chen, Y.-F. Lin and W.-Y. Yeh, *Chem. Eur. J.* 2014, **20**, 936 – 940.

A novel complex that contains two open-cage fullerenes coordinated to a single nickel(II) ion.

As shown in Scheme 8, the open-cage fullerene **ZXG-9** reacts with $NiCl_2$•nH_2O in the presence of sodium carbonate to form the six-coordinate complex, **ZXG-10**. [51] This process involves the cleavage of a C-N bond in **ZXG-9** to form a primary amine that coordinates the nickel ion. The nickel ion is bonded to two oxygen atoms and an amine nitrogen from each fullerene. **ZXG-10** appears to be paramagnetic, since it does not exhibit an informative ^1H or ^{13}C spectrum and six-coordinate Ni(II) complexes are generally paramagnetic. It would be interesting to examine the electrochemical properties of this novel molecule in which two open-cages are linked through a nickel ion.



Scheme 8 The formation of the six-coordinate Ni(II) complex **ZXG-10** from open-cage **ZXG-9** through C-N bond breaking. The black circles show the positions of *t*-BuOO addends on the cages. Adapted from Z. Zhou, N. Xin and L. Gan, *Chem. Eur. J.* 2018, **24**, 451 – 457.

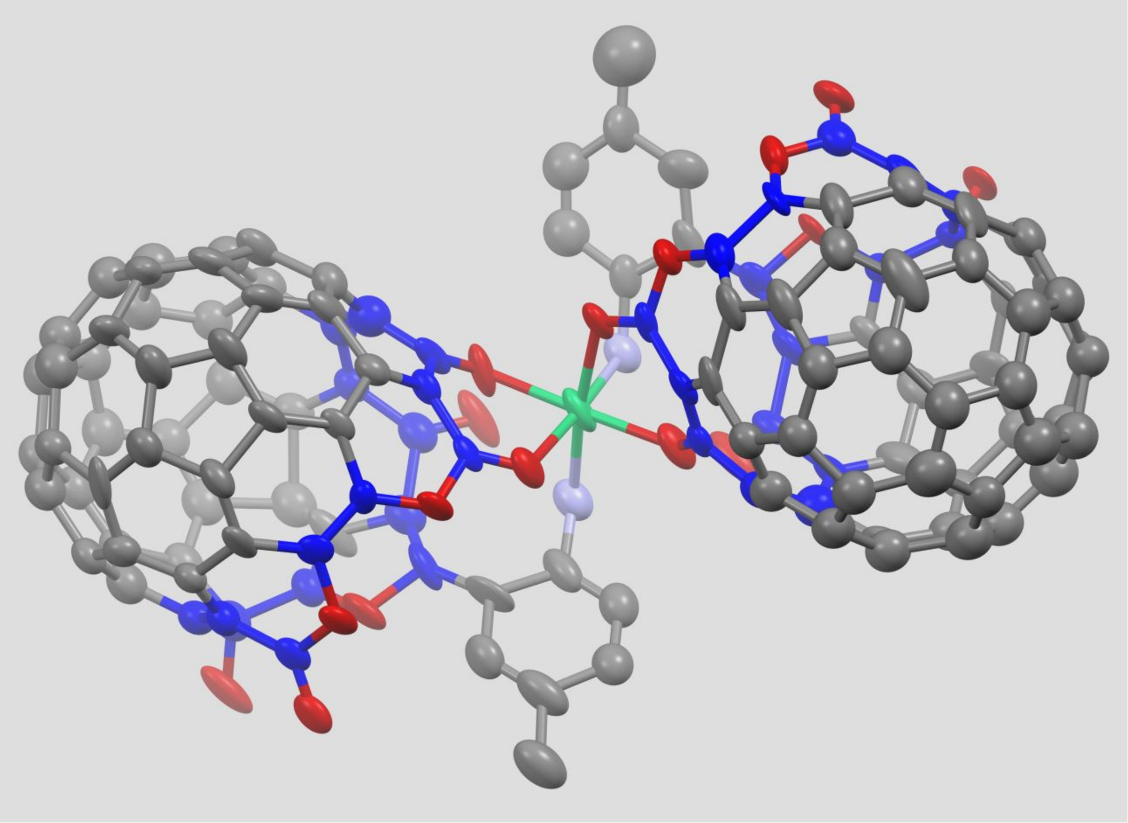


Fig. 13. The structure of **ZXG-10**. Hydrogen atoms, solvate molecules and the two disordered *t*-butylperoxy groups on the back side of the molecule were omitted for clarity. Color scheme: Ni, green; C, dark grey or deep blue if on the perimeter of the cage opening; O, red; N, light blue. From data in Z. Zhou, N. Xin and L. Gan, *Chem. Eur. J.* 2018, **24**, 451 – 457.

Utilization of the interior space of open-cage fullerenes in bonding alkali metal halides.

Gan and coworkers have prepared an open-cage fullerene with a 19-membered orifice that is able to allow halide ions to enter the cavity. [52] Fig. 14 shows drawings of the product of halide insertion, **SLCGYQSG-$Na_2[Br@7]_2\cdot(CH_3OH)_4$**. In the crystal, the complex is a centrosymmetric dimer. The asymmetric unit is shown at the top of this figure. Within this unit, a bromide ion resides at the center of the open-cage, while a sodium ion is coordinated to three oxygen atoms from the cage and to two methanol molecules. Dimerization allows each sodium ion to bond with two additional oxygen atoms from keto groups on the adjacent open-cage, so that each sodium ion is coordinated by a total of seven oxygen atoms. In addition to bromide ion, fluoride, chloride or iodide ions could be introduced to the interior of this empty-cage fullerene. Encapsulation of each ion was achieved through treatment of the open-cage fullerene in *o*-dichlorobenzene solution with a mixture of the hydrohalic acid and acetic acid at temperatures between 60 and 90 ° C. The interior of an open-cage fullerene is electron deficient, which provides the driving force for halide ion encapsulation.

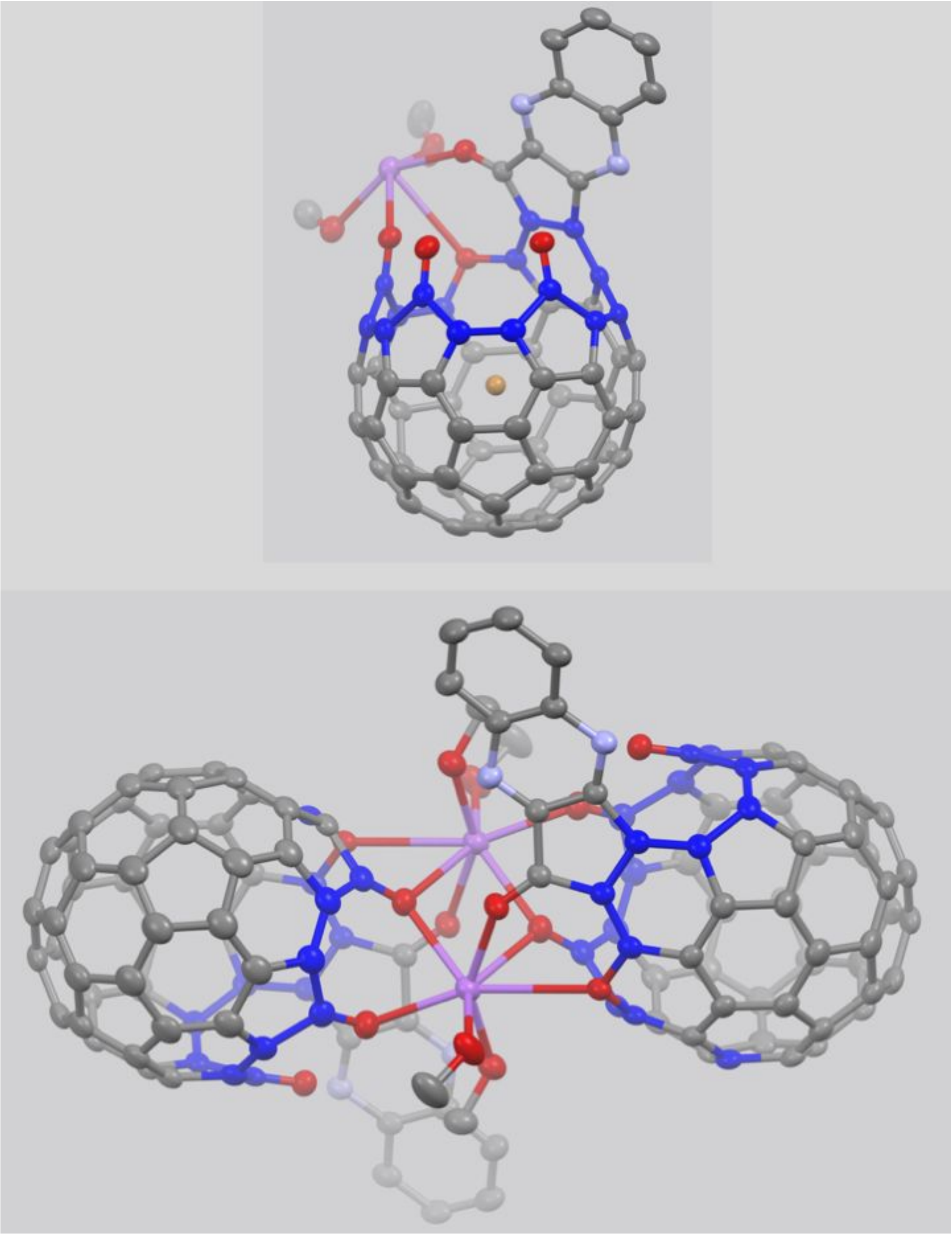


Fig 14. The structure of **SLCGYQSG-Na$_2$[Br@7]$_2$·(CH$_3$OH)$_4$**. Top, the asymmetric unit. Bottom, the centrosymmetric dimer with the interior bromide ion removed for claity. Color scheme: Na, pink; C, dark grey or deep blue if on the perimeter of the cage opening; O, red; N, light blue. From data in S. Sun, Z. Liu, F. Colombo, R. Gao, Y. Yu,Y. Qiu, J. Su and L. B. Gan, *Angew. Chem. Int. Ed*. 2022, **61**, e20221209.

Gan and co-workers have also designed and synthesized a novel open-cage fullerene, **GLLLSG6**, that has a coordinating OH group pointing toward the empty cavity.[53] This arrangement was created to facilitate the entry of metal ions into the open-cage fullerene. Reaction of **GLLLSG6** with lithium fluoride in a mixture of 1,1,2,2-tetrachloroethane and ethanol yields crystals of **GLLLSG-LiF@6**. Fig. 15 shows the structure of **GLLLSG-LiF@6**, which is reported to have an LiF group bound within the cavity of this open-cage fullerene. The crystallographic data have been interpreted to indicate that the crystal contains a mixture of 8 % of the open-cage fullerene, 34 % of the open-cage fullerene with water inside, and 58 % of the open-cage with LiF inside. The reported Li-F distance is 1.31 Å, which seems quite short given the sum of the ionic radii for Li^+ and F^- is 2.09 Å.[54] Shorter Li-F distances in the range 1.77-1.81 Å have been observed in some metallacrown complexes.[55,56] Oddly, the ^{7}Li NMR spectrum of **GLLLSG-LiF@6** showed a single resonance, while the ^{19}F NMR spectrum displayed three resonances. No Li-F coupling was reported. In contrast, the metallacrown complexes of LiF show Li-F coupling in their ^{7}Li and ^{19}F NMR spectra.[55,56] A compound similar to **GLLLSG-LiF@6** with a BeF+ unit entrapped within this same open-cage has also been reported, but salts containing larger ions - NaF, MgF_2, CaF_2, and NaCl - could not enter this open-cage fullerene.[53]

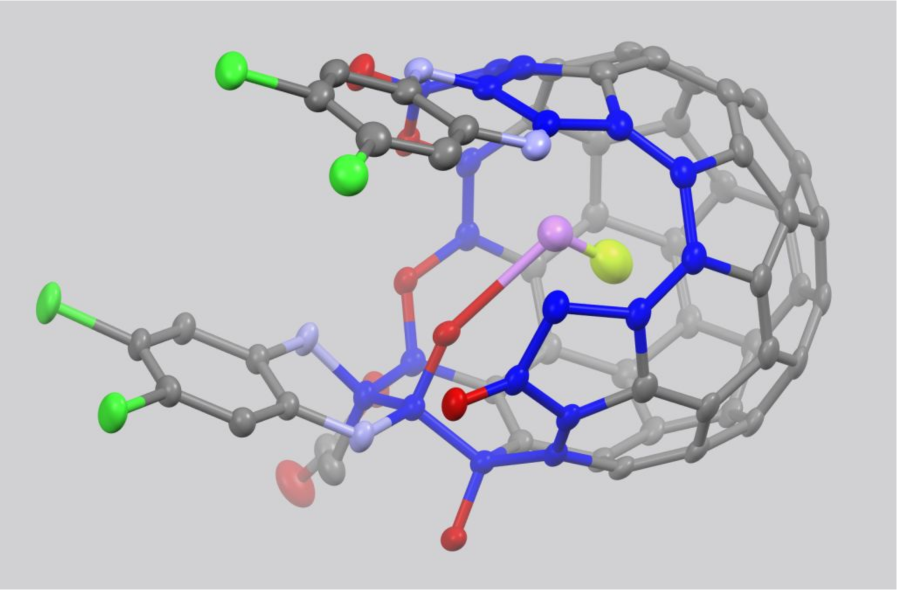


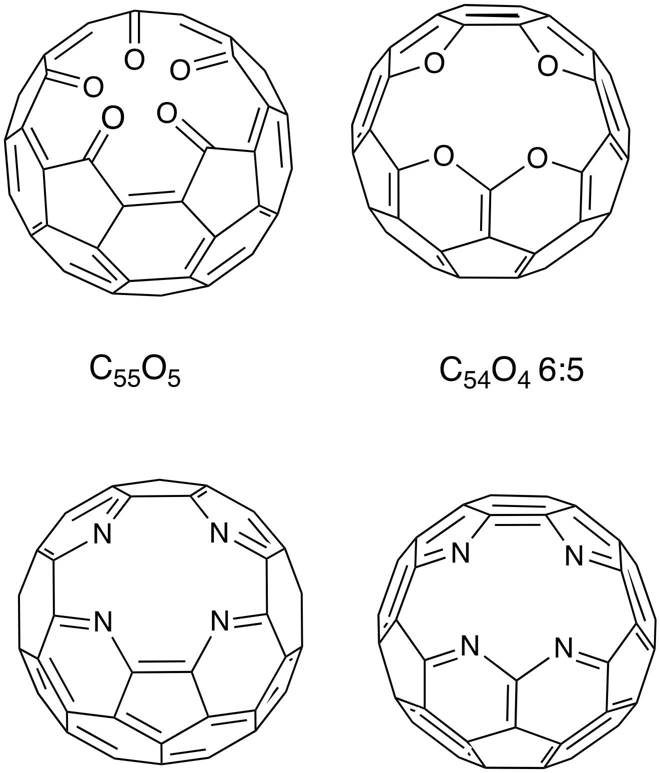
Fig. 15. The structure of **GLLLSG-LiF@6**. Hydrogen atoms and solvate molecules were omitted for clarity. Color scheme: Li, violet; F, yellow; C, dark grey or deep blue if on the perimeter of the cage opening; O, red; N, light blue; Cl, green. From data in R. Gao, Z. Liu, Z. Liu, T. Liang, J. Su, L. Gan, *Angew. Chem. Int. Ed*. 2023, **62**, e202300151.

For comparison, the neutral endohedral, Li@C_{60}, has been produced by ion implantation through Li^+ bombardment into a film of C_{60}.[57] Oxidation of Li@C_{60} yields the salt (Li@C_{60})-($SbCl_6$), which has been examined by single crystal X-ray diffraction.[58] The structure of (Li@C_{60})($SbCl_6$) shows that the lithium ion is not centered within the cage, but is situated near the wall of the cage.

A number of other cases of binding of alkali metal ions to open-cage fullerenes have been reported, but, unfortunately, no crystallographic data concerning their structures are available.[59]

Macrocyclic ligands based upon fullerene cores.

The fullerene cage presents a novel framework for the construction of new macrocyclic ligands. For example, Gan suggested that replacement of five carbon atoms in a pentagon of C_{60} with five oxygen atoms to form keto groups should produce the macrocyclic compound $C_{55}O_5$ as seen in Scheme 9.[60] Li and Gan have expanded upon this idea and have proposed the synthesis of a range of other macrocyclic ligands based upon C_{60} cores by the removal of some carbon atoms and replacement of other carbon atoms with nitrogen or oxygen atoms.[61] A few of these ligands are shown in Scheme 9.

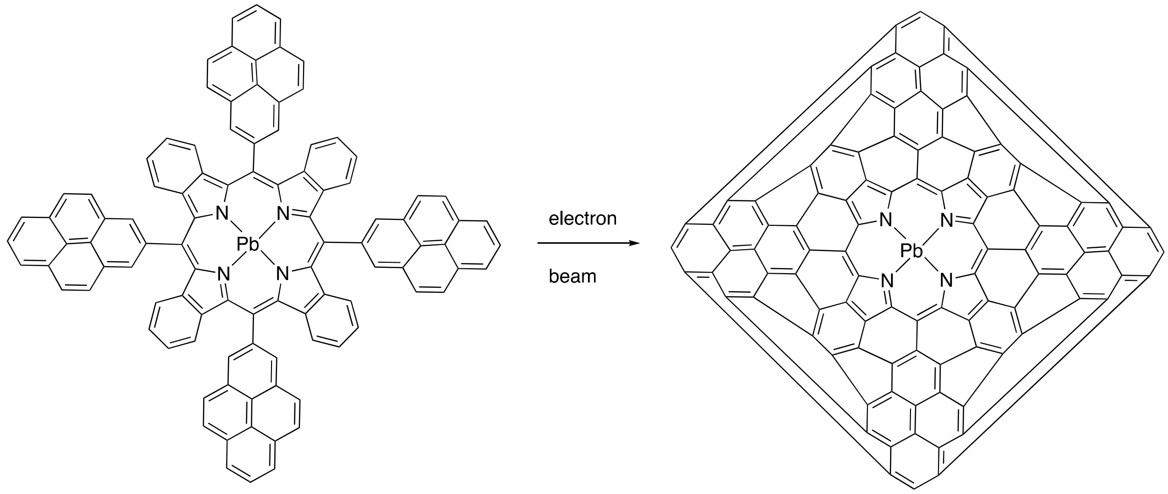


$C_{55}O_5$ $C_{54}O_4$ 6:5

$C_{54}N_4$ 6:6 $C_{54}N_4$ 6:5

Scheme 9 Potential macorcyclic ligands obtained from C_{60} by selective replacement or removal of fullerene carbon atoms with nitrogen or oxygen atoms.

Proceeding along the opposite direction, a macrocyclic ligand has been used to construct an open-cage metallo-azafullerene.[62] As monitored by electron microscopy, the lead porphyrin shown in Scheme 10 was subjected to an electron beam that caused the formation of 24 new carbon-carbon bonds and the creation of a new bowl-shaped molecule. It will be interesting to see if more traditional chemical or thermal methods can be used to make macroscopic amounts of this open-cage metallo-azafullerene.



Scheme 10 Electron beam synthesis of an open-cage metallo-azafullerene.

Conclusions.

Open-cage fullerenes have been demostrated to be complex, chemically reactive ligands. From the results described above, a few generalizations can be made.

Reactions of open-cage fullerenes with metal complexes frequently result in bond breaking within the open-cage fullerene. In many cases, such reactions lead to expansion of the orifice size through carbon-carbon bond breaking as seen in Schemes 2, 5, 6 (reaction b), and 7. In contrast, reaction a in Scheme 6 results in a reduction of the orifice size due to the formation of a new carbon-

carbon bond. The reaction in Scheme 8 also involves bond breaking within the open-cage fullerene, but in this case a carbon-nitrogen bond is cleaved.

The rim carbon atoms of open cage fullerenes are particularly succeptible to addition of $(Ph_3P)_2M$ (M = Pd, Pt) units. Figs. 6 – 8 show examples. In these addition reactions, the open-cage fullerene undergoes only minor structural changes to accommodate the η^2-coordination of the metal to one of the double bonds of the rim. Unlike $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$, these $(Ph_3P)_2M$ adducts are remarkably stable to air and chromatography. In a different vein, a $(Ph_3P)_2Pt$ unit has been inserted into a carbon-carbon bond on the rim of an open-cage fullerene as seen in Scheme 2 and Fig. 5.

Anionic forms of open-cage fullerenes frequently form dimers in which pairs of Ag^+ or Na^+ ions connect the two cages through coordination to oxygen atoms on the cage surface. Relevant examples include **$\{MMK\text{-}9\text{-}(OCH_3)_5Ag(AgO_2CCF_3)\}_2$** as seen in Fig. 3, the polymer, **$[\{MMK\text{-}9(OCH_3)_5Ag(AgOCH_3)\}_2\bullet H_2O]_n$** as shown in Fig. 4, **GLLSG-3** as displayed in Fig. 8, and **$SLCGYQSG\text{-}Na_2[Br@7]_2\cdot(CH_3OH)_4$** as shown in Fig 14. The nickel complex, **ZXG-10**, can be viewed similarly with a single Ni^{2+} ion connecting the two anionic open-cage fullerenes as seen in Figure 13.

Much remains to be learned about the interactions of open-cage fullerenes with metal complexes. Can metal ions larger than Li^+ be encouraged to enter the interior of these open cages? How will redox processes alter the structures of metal complexes of open-cage fullerenes? Will oxidation lead to the ejection of encapsulated anions? Will reduction of the cage encourage movement of metal ions into the interior void? The research reported here all involves open-cage fullerenes prepared from C_{60}, but open cage-fullerenes can also be made from larger cages such as C_{70} and C_{84}. Will these larger cages provide a more spacious interior void to host various guests?

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