with TES buffer (pH 7.5) containing 20% ethanol. The HLADH cross-linked crystals were stored in 50 mM TES buffer (pH 7.5).

Stability of NAD$^+$ and NADH in buffer: Solutions (20 mM) of NAD$^+$ or NADH were incubated at 30 °C in 50 mM TES/HEPES buffer at pH 6, pH 7 and pH 8. Additionally, 20 mM NAD$^+$ or NADH was incubated at 30 °C in 25 mM sodium phosphate buffer at pH 6 and pH 8. Incubations were performed in duplicate. Active cofactor was quantified enzymatically. A 100-µL aliquot of 20 mM cofactor solution was removed at intervals and added to 900 µL of TES buffer (50 mM, pH 7.5) at 30 °C containing 10 µmol substrate and 2 mg of HLADH. The substrate for reduced cofactor was cinnamaldehye and the substrate for oxidized cofactor was cinnamyl alcohol. Moles of product formed were measured by HPLC and assumed to be proportional to moles of active cofactor added to the reaction. (HPLC conditions: 15 cm Rainin $C_{18}$ microsorb 5 µ 300 A column; mobile phase: acetonitrile/water = 1/1; flow rate: 0.5 mL min$^{-1}$; monitoring at 260 nm; retention time = 2.38 (cinnamyl alcohol); 2.97 min (cinnamaldehyde). Standard curves were constructed from known quantities of cofactor. Data is presented as a percentage of the initial cofactor quantity (20 µmol).

Stability of HLADH in buffer: HLADH (2 mg mL$^{-1}$) was incubated at 30 °C in 50 mM HEPES/TES buffer at pH 6, pH 7, and pH 8 and also in 25 mM phosphate buffer at pH 6 and pH 8. Aliquots (50 µL) were removed at intervals and enzyme activity was measured in a cosubstrate assay of 20 mM cinnamaldehyde, 1.5 M isopropanol, and 100 mM NAD$^+$ in 50 mM HEPES/TES buffer at 30 °C. The rate of product formation was measured by HPLC. Data is presented as a percentage of the initial activity.

Stability of HLADH-NADH-CLEC in buffer: HLADH-NADH-CLEC (10 mg mL$^{-1}$) was incubated at 30 °C in 50 mM HEPES/TES buffer at pH 6 and pH 8 and in 25 mM phosphate buffer at pH 6 and pH 8. Aliquots (50 µL) were removed at intervals and enzyme activity was measured in a cosubstrate assay of 20 mM cinnamaldehyde and 1.5 M isopropanol in 50 mM HEPES/TES buffer at 30 °C. The rate of product formation was measured by HPLC. Data is presented as a percentage of the initial activity.

General procedure for reductions: A suspension of substrate (20 µL) in a mixture of isopropanol (0.2 mL) and phosphate buffer (2 mL, pH 7.0) was incubated with 200 µL of CLEC or soluble HLADH at room temperature with and without adding 0.3 mg of NADH. The conversion was determined by GC analysis. Conditions for GC analysis: Cyclodex B capillary GC 25 m × 0.25 mm column, thickness: 0.25 µm (J & W Scientific, Folsom, CA), flow rate: He, 1 mL min$^{-1}$; temperature program: initial: 90 °C for 10 min, gradient rate: 2–5 °C min$^{-1}$, final: 160 °C for 0 min).

HLADH-NADH-CLEC-I catalyzed multi-cycle reaction of cinnamaldehyde: A slurry of CLEC (10 mL, 50 mg dry weight) and 0.5 g of silica gel in a solution containing 100 mM Tris HCl and 0.1 mM $ZnCl_2$ (pH 9.0) was packed in a 10 mm × 10 cm column (Pharmacia C). A solution of 200 mM 1,4-butanediol and 10 mM cinnamaldehyde in 100 mM Tris HCl and 0.1 mM $ZnCl_2$ buffer (pH 9.0) was pumped though the column at a flow rate of approximately 15 mL h$^{-1}$ at ambient temperature. Conversion of aldehyde was measured by HPLC analysis using a 15-cm Rainin $C_{18}$ microsorb 5 µ 300 A column (mobile phase: acetonitrile/water = 1/1; flow rate: 0.5 mL min$^{-1}$; monitoring at 260 nm; retention time: 2.38 min (product); 2.97 min (substrate)). A total substrate volume of 3.22 L passed though the column before the experiment was stopped.

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[1] a) C.-H. Wong, G. M. Whitesides, *J. Am. Chem. Soc.* **1981**, *103*, 4890–4899; b) C.-H. Wong, G. M. Whitesides, *Enzymes in Synthetic Organic Chemistry*, Pergamon, **1994**, chap. 3, pp. 131–195.

[2] C. Schmidt-Dannert, F. H. Arnold, *Trends Biotechnol.* **1999**, *17*, 135–136.

[3] V. V.Mozhaev, *Trends Biotechnol.* **1993**, *11*, 88–95.

[4] Recent reviews: a) A. L. Margolin, *Trends Biotechnol.* **1996**, *14*, 223–230; b) T. Zelinski, H. Waldmann, *Angew. Chem.* **1997**, *109*, 746–748; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 722–724; c) J. J. Lalonde, *CHEMTECH* **1997**, *27*, 38–45; d) D. Haring, P. Schreier, *Curr. Opin. Chem. Biol.* **1999**, *3*, 35–38.

[5] a) N. L. St. Clair, M. A. Navia, *J. Am. Chem. Soc.* **1992**, *114*, 7314–7316; b) J. J. Lalonde, C. P. Govardhan, N. K. Khalaf, O. G. Martinez, K. J. Visuri, A. L. Margolin, *J. Am. Chem. Soc.* **1995**, *117*, 6845–6852; c) R. A. Persichetti, N. L. St. Clair, J. P. Griffith, M. A. Navia, A. L. Margolin, *J. Am. Chem. Soc.* **1995**, *117*, 2732–2737; d) Y.-F. Wang, K. Yakovlevsky, B. Zhang, A. L. Margolin, *J. Org. Chem.* **1997**, *62*, 3488–3495; e) L. Z. Vilenchik, J. P. Griffith, N. St. Clair, M. A. Navia, A. L. Margolin, *J. Am. Chem. Soc.* **1998**, *120*, 4290–4294.

[6] K. M. Lee, M. Blaghen, J.-P. Samama, J.-F. Biellmann, *Bioorg. Chem.* **1986**, *14*, 202.

[7] a) H. Eklund, C. I. Branden, *J. Biol. Chem.* **1979**, *254*, 3458–3461; b) H. Eklund, J. P. Samama, L. Wallen, C. I. Branden, A. Akeson, T. A. Jones, *J. Mol. Biol.* **1981**, *146*, 561–587; c) H. Eklund, B. V. Plapp, J. P. Samama, C. I. Branden, *J. Biol. Chem.* **1982**, *257*, 14349–14358; d) H. Eklund, J. P. Samama, T. A. Jones, *Biochemistry* **1984**, *23*, 5982–5996.

[8] C.-H. Wong, D. G. Drueckhammer, H. M. Sweers, *J. Am. Chem. Soc.* **1985**, *107*, 4028.

[9] E. Keinan, E. K. Jafeli, K. K. Seth, R. Lamed, *J. Am. Chem. Soc.* **1986**, *108*, 162.

[10] H. Eklund, *Pharmacol. Biochem. Behav.* **1983**, *18*, 73–81.

[11] S. B. Sobolov, M. D. Leonida, A. Bartoszko-Malik, K. I. Voivodov, F. McKinney, J. Kim, A. J. Fry, *J. Org. Chem.* **1996**, *61*, 2125.

[12] W. Hummel, M.-R. Kula, *Eur. J. Biochem.* **1989**, *184*, 1–13.

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# $In_8(C_6H_3\text{-}2,6\text{-}Mes_2)_4$ (Mes = $C_6H_2\text{-}2,4,6\text{-}Me_3$): A Metal-Rich Main-Group Cluster with a Distorted Cubane Structure[**]

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The reaction between indium monochloride and the bulky lithium terphenyl $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$[1] (Trip = $C_6H_2\text{-}2,4,6\text{-}i\mathrm{Pr}_3$) was recently reported to yield the monomeric compound $InC_6H_3\text{-}2,6\text{-}Trip_2$.[2a] This compound and its thallium analogue[2b] are unique examples of one-coordinate metal atoms in the solid state. Reactions of InCl or TlCl with less crowded lithium terphenyls are expected to lead to more highly aggregated structures, which may involve interesting metal–metal interactions. This class of compounds is of considerable current interest in Group 13 metal chemistry.[3] We therefore investigated the reactions of InCl with lithium terphenyls of various sizes.[4] Initial work focused on the less crowded ligand $C_6H_3\text{-}2,6\text{-}Mes_2$[5] (Mes = $C_6H_2\text{-}2,4,6\text{-}Me_3$). Here we report that the reaction of $LiC_6H_3\text{-}2,6\text{-}Mes_2$ with InCl leads to the unusual cluster species $In_8(C_6H_3\text{-}2,6\text{-}Mes_2)_4$ (**1**) rather than the projected stoichiometric aggregates of formula $(InC_6H_3\text{-}2,6\text{-}Mes_2)_n$ ($n \geq 2$).

Compound **1** was synthesized by treating a suspension of InCl in THF with $LiC_6H_3\text{-}2,6\text{-}Mes_2$ at about −78 °C. Red crystals of **1** were isolated in approximately 25% yield after recrystallization from hexane. The X-ray crystal structure[6] of **1** (Figure 1) shows that in the solid state the compound has a

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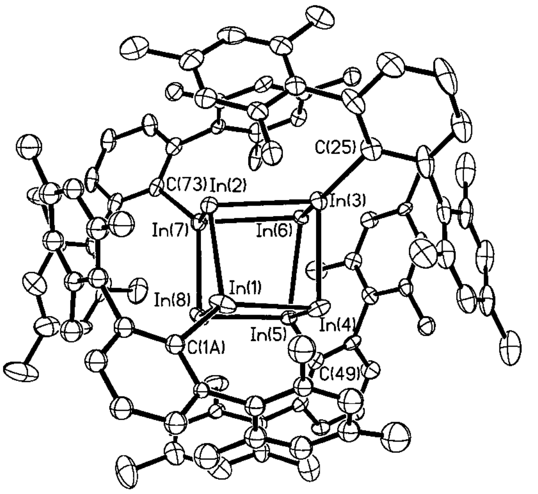

Figure 1. Schematic drawing of **1** (H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: In(1)–In(2) 2.8754(13), In(1)–In(4) 2.8814(13), In(1)–In(8) 2.9328(13), In(1)–C(1A) 2.216(18); In(2)-In(1)-In(4) 89.02(3), In(2)-In(1)-In(8) 73.59(3), In(4)-In(1)-In(8) 75.57, In(1)-In(2)-In(3) 81.28(3), In(1)-In(2)-In(7) 106.54(4), In(3)-In(2)-In(7) 104.96(3).

distorted cubane arrangement of eight indium atoms. However, only four of the metal atoms carry a terphenyl substituent. The geometrical distortions in the $In_8$ array result in approximate $D_{2d}$ local symmetry, similar to that of several other cubane compounds.[7] The structure may be regarded as consisting of two interpenetrating tetrahedra of four $InC_6H_3$-2,6-$Mes_2$ units and four indium atoms. It seems probable that each $InC_6H_3$-2,6-$Mes_2$ moiety donates two electrons to In–In bonding in the $In_8$ unit, whereas each unsubstituted indium atom supplies one electron, and the remaining two valence electrons are accommodated in a nonbonding orbital that is mostly 5s in character. Thus, twelve electrons may be available for cluster bonding in this scheme. Although the formal In–In bond order in the cube is predicted to be 0.5, the average In–In distance is 2.915(26) Å (range 2.857(4)–2.966(4) Å), which is comparable to In–In single-bond lengths in some $R_2InInR_2$[8] species and is considerably shorter than the In–In distances (3.25, 3.38 Å) in indium metal.[9] The average In–C distance in **1** of 2.205(12) Å is shorter than those of 2.260(7) and 2.250(5) Å in $InC_6H_3$-2,6-$Trip_2$[2a] and $\{InC(SiMe_3)_3\}_4$, respectively.[10]

The shortening of In–C bonds on complexation of InR units with the metal atoms was commented upon previously[2a] and it may be connected with changes in metal orbital hybridization or metal charge. For example, if in the case of **1**, the $InC_6H_3$-2,6-$Mes_2$ units behave as electron donors to the indium atoms, ionic character would develop across the In–In bond, that is, $In^{\delta-}$-$In^{\delta+}$-$C_6H_3$-2,6-$Mes_2$. This should result in a shortening of the In–C bonds consistent with experimental observations. Interestingly, there are no other close interactions between the metal atoms and the ligands. The closest approaches of the centroids of *ortho*-mesityl rings to the unsubstituted indium atoms In(2), In(4), In(6), and In(8) are in the range 3.631–4.036 Å. These may be compared to the corresponding distances of 2.83 and 2.89 Å in the contact ion pair complex $[In(mesitylene)_2][InBr_4]$.[11] Clearly, the "solvation" of the unsubstituted indium atoms in **1** by the *ortho*-mesityl groups is very weak. This suggests that the stability of **1** depends upon the steric protection afforded to the $In_8$ core by the $C_6H_3$-2,6-$Mes_2$ substituents rather than dipolar interactions between the *ortho*-mesityl groups and the indium atoms. This conclusion is also consistent with the proposed ionic character of the In–In bonds, which gives rise to negative charge at the unsubstituted indium atoms and hence reduced likelihood of interactions between the mesityl groups and these centers.

At present few neutral, donor-free, cluster compounds of heavier Group 13 elements are known.[12] For indium, apart from the tetraorganodimetallic species mentioned above, there are the weakly dimerized complex (In–In 3.631(2) Å) $[In\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$,[13] the tetrameric $[In\{C(SiMe_3)_3\}_4$[10] (In–In 3.002(1) Å), and the weakly bonded hexamer $[In(\eta^5\text{-}C_5Me_5)]_6$[14] (In–In 3.942(1)–3.963(1) Å), all of which have a substituent on each indium atom. In addition, there is the unusual complex $In(InTrip_2)_3$[8d], in which the central metal atom is bound to three $In(Trip)_2$ groups. Stoichiometrically, however, the complexes most relevant to **1** are the recently reported clusters $In_{12}\{Si(t\text{Bu})_3\}_8$[15] and $In_8\{Si(t\text{Bu})_3\}_6$.[16] The $In_{12}$ cluster can be described as a *conjuncto*-indane composed of two distorted octahedral $In_6\{Si(t\text{-Bu})_3\}_4$ moieties which are linked by In–In bonds across the two unsubstituted indium atoms in each octahedral unit. The particular stability of $In_{12}\{Si(t\text{Bu})_3\}_8$, whose In–In bond lengths are similar to those in **1**, was attributed to steric effects of the $Si(t\text{Bu})_3$ groups, which completely obscure the surface of the $In_{12}$ array from attack. A space-filling model of **1** (Figure 2) clearly shows that the $C_6H_3$-2,6-$Mes_2$ ligand accomplishes the same end for the $In_8$ array in **1**. The structure of $In_8\{Si(t\text{Bu})_3\}_6$ bears an even closer resemblance to **1** in that also it has an $In_8$ cubane core. In this case the core is stretched along a diagonal and may be classified as a doubly capped octahedral compound. Similarly, **1** can be described as a tetracapped tetrahedron. The structural data for these three clusters, analogues of which are unknown in boron chemistry, indicate that, in principle at least, it should be possible to control the size and geometry of indium clusters by means of the steric properties of the

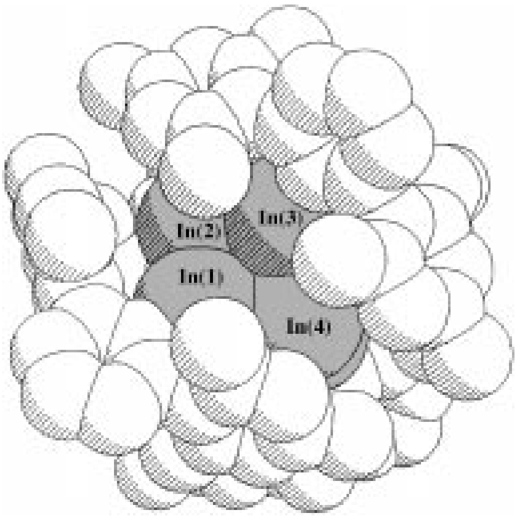

Figure 2. Space-filling drawing of **1** illustrating the steric protection of the $In_8$ core by the $C_6H_3$-2,6-$Mes_2$ ligands.

substituents on the indium atoms. The synthesis and structure of **1** also suggest that the extrusion of part of the ligand array in simple clusters such as $R_2MMR_2$ (M = Ga, In) or $(InR)_n$ to give higher clusters that incorporate unsubstituted metal atoms may be a general phenomenon in these sterically crowded species. Another distinctive feature of the synthesis of **1** is that an In$^I$ compound was employed as starting material. This already has a 1:1 metal:ligand ratio and is closer stoichiometrically to the more highly aggregated cluster product **1** than are the higher valent starting materials, which usually carry two substituents per metal atom. It now seems likely that further examples of these interesting species will be isolated not only for indium but also for the other Group 13 metals.

## *Experimental Section*

Under anaerobic and anhydrous conditions, a pale yellow solution of LiC$_6$H$_3$-2,6-Mes$_2$ (1.60 g, 4.99 mmol) in THF (20 mL) was cooled to ca. $-78\,^\circ$C and added dropwise to a yellow suspension of InCl (0.82 g, 5.5 mmol) in THF (5 mL) at ca. $-78\,^\circ$C. The solution became dark orange-brown upon addition and was stirred for 30 min. The solution was warmed to $-15\,^\circ$C, and the THF was removed under reduced pressure. The orange-brown solid was extracted with hexanes (100 mL) and gravity filtered through a Celite pad. The volume of the orange-brown solution was reduced to 30 mL. Cooling to ca. $0\,^\circ$C for 12 h produced dark brown crystals of **1** (0.55 g, 0.25 mmol, 36.8% yield based on InCl). M.p. 207–210 °C; $^1$H NMR (399.77 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 0.88$ (t, hexane), 1.22 (m, hexane), 1.88 (s, 24 H, *p*-Me, Mes), 2.12 (brs, 24 H, *o*-Me, Mes), 2.29 (brs, 24 H, *o*-Me, Mes), 6.75 (d, $^3J$ (H, H) = 7.2 Hz, 8 H, *m*-C$_6$H$_3$), 6.86 (s, *m*-Mes, 16 H), 7.05 (t, $^3J$(H, H) = 7.2 Hz, 4 H, *p*-C$_6$H$_3$); $^{13}$C{$^1$H} NMR (100.53 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 21.29$ (*p*-Me, Mes), 21.65 (*o*-Me, Mes), 129.28 (*m*-Mes), 136.59 (*m*-C$_6$H$_3$), 137.13 (*o*-Mes), 137.23 (*p*-C$_6$H$_3$), 141.53 (*p*-Mes), 144.97 (*i*-Mes), 148.77 (*o*-C$_6$H$_3$), 189.88 (*i*-C$_6$H$_3$); UV/Vis (hexanes): $\lambda_{max}$ ($\varepsilon$) = 305sh (1000).

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[1] B. Schiemenz, P. P. Power, *Organometallics* **1998**, *15*, 958.

[2] a) S. T. Haubrich, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 2202; b) M. Niemeyer, P. P. Power, *Angew. Chem.* **1998**, *110*, 1291; *Angew. Chem. Int. Ed.* **1998**, *37*, 1277.

[3] W. Uhl, *Angew. Chem.* **1993**, *105*, 1449; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1386; C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 129.

[4] B. T. Twamley, S. T. Haubrich, P. P. Power, *Adv. Organomet. Chem.* **1999**, *44*, 1.

[5] K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehnschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11353.

[6] Crystal data for **1** (190 K) with Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation: $a = 14.0174(5)$, $b = 15.5917(5)$, $c = 23.7818(8)$ Å, $\alpha = 92.047(1)$, $\beta = 104.734(1)$, $\gamma = 107.703(1)^\circ$, $Z = 2$, space group $P\bar{1}$, $R_1 = 0.052$ for 7389 data with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135535. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] For example: K. S. Hagen, J. G. Reynolds, R. H. Holm, *J. Am. Chem. Soc.* **1981**, *103*, 4054; B.-K. Teo, J. C. Calabrese, *J. Am. Chem. Soc.* **1975**, *97*, 1256.

[8] a) W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139; b) R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, M. R. Bond, C. J. Carrano, *J. Am. Chem. Soc.* **1993**, *115*, 2070; c) N. Wiberg, K. Amelunxen, H. Nöth, H. Schmidt, H. Schwenk, *Angew. Chem.* **1996**, *108*, 110; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 65; d) P. J. Brothers, K. Hübler, U. Hübler, B. C. Noll, M. M. Olmstead, P. P. Power, *Angew. Chem.* **1996**, *108*, 2528; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2355.

[9] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon, Oxford, **1984**, p. 1278.

[10] W. Uhl, A. Jantschak, W. Saak, M. Kaupp, R. Wartchow, *Organometallics* **1998**, *17*, 5009.

[11] J. Ebenhöch, G. Müller, J. Riede, H. Schmidbaur, *Angew. Chem.* **1984**, *96*, 367; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 386.

[12] Some prominent recent examples for Al and Ga are given in: A. Ecker, L. Weckert, H. Schnöckel, *Nature* **1997**, *387*, 379; C. Klemp, R. Koppe, E. Weckert, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 1851; *Angew. Chem. Int. Ed.* **1999**, *38*, 1740; W. Kostler, G. Linti. *Angew. Chem.* **1997**, *109*, 2758; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2644.

[13] H. Schumann, C. Janiak, F. Görlitz, J. Loebel, A. Dietrich, *J. Organomet. Chem.* **1989**, *363*, 243.

[14] O. T. Beachley, R. Blom, M. R. Churchill, J. Fettinger, J. C. Pazik, L. Victoriano, *J. Am. Chem. Soc.* **1986**, *108*, 4666.

[15] N. Wiberg, H.-W. Lerner, H. Nöth, W. Ponikwar, *Angew. Chem.* **1999**, *111*, 887; *Angew. Chem. Int. Ed.* **1999**, *38*, 839.

[16] N. Wiberg, T. Blank, A. Purath, G. Stösser, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 2745; *Angew. Chem. Int. Ed.* **1999**, *38*, 2563.

# The Synthesis of a Novel Strained Diyneparacyclophane and Its Dimer by Metal-Mediated Coupling**

Shawn K. Collins, Glenn P. A. Yap, and Alex G. Fallis*

Diverse families of cyclophanes[1] and assorted cage compounds[2] with novel structures and properties continue to be topics of wide-spread interest.[3] Earlier, we reported the synthesis of a novel class of enediyne cyclophanes by sequential palladium- or copper-mediated coupling.[4] In contrast to normal [n.m]paracyclophanes, the rotation of the benzene ring in these molecules is not restricted by the bridging bonds. Consequently they were christened revolveneynes **1** as the aromatic rings rotate freely, with "skipping rope"-type properties, in which the bridging units and one aromatic ring may swing around each other. The unsaturated bonds in these bridges impart a helical twist to the structures. As a result, they possess helical chirality, a property that is shared with related $D_2$-symmetric olefinic paracyclophanes.[5] In a related area, we[6] and others[7] have attemped to extend these syntheses to multibridged systems in order to prepare potential precursors to fullerenes such as $C_{60}$, but with limited success. However, Vollhardt and co-workers[8] have demonstrated that **2** decomposed explosively to form carbon onions when heated, and cobalt alkyne complexes afforded carbon nanotubes.

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