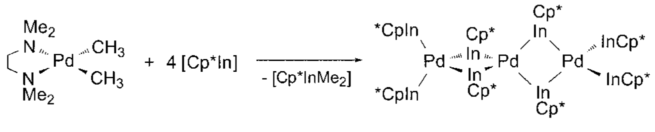
[36] Tie-2: a) P. Stahl, L. Kissau, R. Mazitschek, A. Giannis, H. Waldmann, *Angew. Chem.* **2002**, *114*, 1222–1226; *Angew. Chem. Int. Ed.* **2002**, *41*, 1174–1178; b) L. D. Arnold, D. J. Calderwood, R. W. Dixon, D. N. Johnston, J. S. Kamens, R. Munschauer, P. Rafferty, S. E. Ratnofsky, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2167–2170; c) A. F. Burchat, D. J. Calderwood, G. C. Hirst, N. J. Holman, D. N. Johnston, R. Munschauer, P. Rafferty, G. B. Tometzki, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2171–2174; VEGFR-3: d) V. Kirkin, R. Mazitschek, J. Krishnan, A. Steffen, J. Waltenberger, M. S. Pepper, A. Giannis, J. P. Sleeman, *Eur. J. Biochem.* **2001**, *268*, 5530–5540.

[$Pd_3(InCp^*)_4(\mu_2\text{-}InCp^*)_4$]: Three Linearly Arranged Palladium Atoms Wrapped into a Fluxional Shell of Eight InCp* Ligands**

Tobias Steinke, Christian Gemel, Manuela Winter, and Roland A. Fischer*

In 1999 Murugavel and Chandrasekhar stated in a Highlight article in this journal on monovalent Group 13 organometallic compounds that "the use of these compounds … in transition metal chemistry is likely to have a huge impact on the way new metal–metal bonds are made in the future … and there is no doubt that we will be witnessing the synthesis of a whole range of new cluster types in the future."[1] The monovalent homoleptic complexes [$M\{EC(SiMe_3)\}_4$] (M = Ni, E = Ga; M = Pt, E = In) synthesized by Uhl et al. in 1998[2] and [$Ni(GaCp^*)_4$] (Cp* = pentamethylcyclopentadienide) synthesized by Jutzi et al. in 1999[3] confirmed this statement. Hitherto, most of the studies concerning complexes of these new ligands ER (E = Al, Ga, In, R = Alkyl, Aryl), which are isolobal to CO, were focused on the coordination to transition metal carbonyl fragments [$(CO)_nM_a$],[4,5] a chemistry that has also been stimulated by our work on [$(CO)_4Fe(AlCp^*)$].[6] Constitution and structural characteristics of new [GaCp*]-substituted Ni_4 and Rh_6 carbonyl clusters or [$\{(CpNi)(\mu\text{-}AlCp^*)\}_2$], which were synthesized by Jutzi et al.[7] and Schnöckel et al.,[8] respectively, are directly related to classical transition metal carbonyl cluster structures. Another heuristically valuable analogy of ER ligands to phosphanes is observed for the compounds [$(dcpe)Pt(ER)_2$] (dcpe = bis(dicyclohexyl)phosphanylethane),[9] a series related to [$Pt(PR_3)_4$]. We recently synthesized the Pt_2Ga_5 complex [$Pt_2(GaCp^*)_2(\mu_2\text{-}GaCp^*)_3$] selectively by reaction of [$Pt(\eta^2\text{-}C_2H_4)_3$] and an excess of [GaCp*], and this complex represents the first example of a homoleptic complex of the new series [$M_a(ER)_b$] ($b > a > 1$).[10] No structural analogue is known in carbonyl or phosphane cluster chemistry for this complex. Further investigations of this chemistry led us to the title compound [$Pd_3(InCp^*)_4(\mu_2\text{-}InCp^*)_4$] (**1**).

When [$(tmeda)Pd(CH_3)_2$] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) is treated with an excess of [InCp*] in solution in hexane (Scheme 1), and the reaction mixture is warmed to 60 °C, the trinuclear complex [$Pd_3(InCp^*)_4(\mu_2\text{-}InCp^*)_4$] (**1**) is quantitavely formed, instead of the expected monomeric complex [$Pd(InCp^*)_4$] (**2**). Complex **1** can be crystallized from benzene as large deep red single crystals in reproducible yields of 90%. The molecular structure of **1** (Figure 1) exhibits three edge-bridging $PdIn_4$ tetrahedrons. The three central palladium atoms are arranged with only a small deviation from linearity of 10° (Figure 2). The distortion of the $PdIn_4$ tetrahedrons is expressed in the In-Pd-In angles, which are smaller than 109° for the terminal In atoms (101.3° and 104.0°) and larger than 109° for the bridging In atoms (114.0° to 116.6°). Correspondingly the dihedral angles In3-Pd1-Pd2-In4 and In6-Pd2-Pd3-In5 deviate from planarity (22.34° and 6.67°). The two bridging In atoms that exihibit the higher deviation (In3, In4) are bent towards the site slightly opened by the Pd-Pd-Pd angle, resulting in a butterfly-shaped structure. The terminal Pd–In distances (2.54–2.57 Å) are somewhat shorter than the bridging ones (2.58–2.61 Å); the Pd–In distances around the central Pd2 atom are the longest (about 2.63 Å). In comparison, the Pd–In distances in the intermetallic phase Pd_3In_7, which contains



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Scheme 1. Preparation of **1** from [$Pd(tmeda)(CH_3)_2$] and [Cp*In].

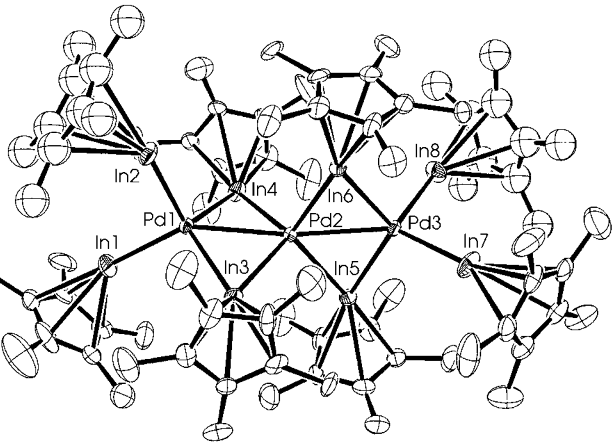

Figure 1. Structure of **1** (ORTEP plot; ellipsoids for 30% probability). Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: $Cp^*_{centroid}$-In1 2.247, $Cp^*_{centroid}$-In2 2.343, $Cp^*_{centroid}$-In3 2.239, $Cp^*_{centroid}$-In4 2.236, $Cp^*_{centroid}$-In5 2.231, $Cp^*_{centroid}$-In6 2.246, $Cp^*_{centroid}$-In7 2.276, $Cp^*_{centroid}$-In8 2.315, $Cp^*_{centroid}$-In1- Pd1 153.8, $Cp^*_{centroid}$-In2- Pd1 147.3, $Cp^*_{centroid}$-In7-Pd3 174.3, $Cp^*_{centroid}$-In8- Pd3 157.0.

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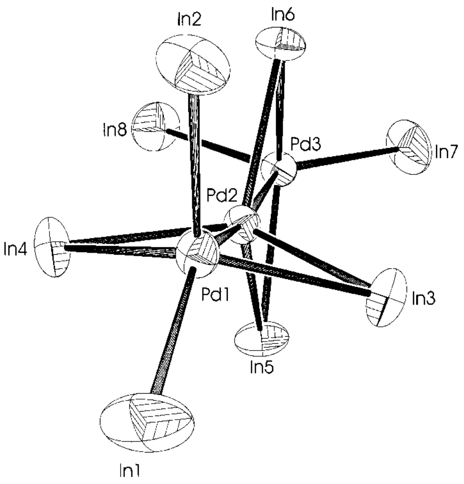
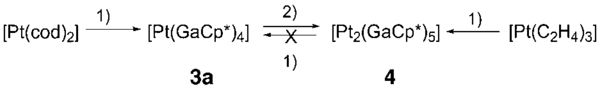


Figure 2. Arangement of the Pd and In atoms in **1** (ORTEP plot; ellipsoids for 50% probability). Selected distances [Å] and angles [°]: Pd1-Pd2 2.7762(14), Pd2-Pd3 2.7747(14), Pd1-In1 2.5397(15), Pd1-In3 2.5831(14), Pd2-In3 2.6319(14), Pd2-In5 2.6258(14), Pd3-In5 2.5962(14), Pd3-In7 2.5520(15); Pd1-Pd2-Pd3 169.52(5), In1-Pd1-In2 101.24(5), In3-Pd1-In4 113.96(5), In3-Pd2-In4 110.70(5), In5-Pd2-In6 114.76(5), In5-Pd3-In6 16.60(5), In7-Pd3-In8 104.00(6), In3-Pd1-Pd2-In4 157.66(6), In6-Pd2-Pd3-In5 173.33(5).

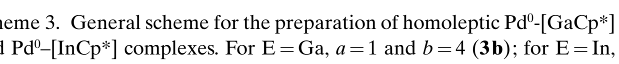
an eight-coordinate palladium center, are 2.76 to 2.79 Å.[12] These Pd–Pd distances of 2.78(1) and 2.77(1) Å do not exclude a bonding Pd^0–Pd^0 interaction. In comparison, the tetranuclear cluster $[Pd_4(CO)_5(PPh_3)_4]$ exhibits a bonding Pd–Pd distance of 2.75–2.77 Å, whereas the nonbonding Pd–Pd distance in the same molecule is 3.21 Å.[13] The In–$Cp^*_{centroid}$ distances are somewhat longer for the terminal (2.28–2.34 Å) than for the bridging ligands (2.23–2.25 Å), and are similar to the distance found in the free ligand (gas phase: 2.29 Å;[14] solid state: 2.30 Å[15]). This is indicative of weakly polar Pd–In bonds, as was also reported for $[(dcpe)Pt(InCp^*)_2]$ (2.28 Å).[9b] In contrast, in $[(CO)_5Cr(InCp^*)]$ the In–$Cp^*_{centroid}$ distance is shorter (2.17 Å).[7a] The Pd-In-$Cp^*_{centroid}$ angles deviate from 180° (144.7–174.3°), but a systematic difference between terminal and bridging ligands is not apparent. These and the other deviations mentioned are probably attributed to steric congestion. A similar situation was found for $[Ni(GaCp^*)_4]$.[3]

The ^1H and the ^{13}C NMR spectrum of **1** at ambient temperature in C_6D_6 exhibits only one signal or one set of signals for the C_5Me_5 ligands, respectively. No decoalescence or broadening of the signals was observed down to −30 °C ([D$_8$]toluene). Evidently, a fast process takes place, in which the terminal and bridging $[InCp^*]$ units are exchanged. At −80 °C a decoalescence of the signal into two signals at $\delta = 2.26$ and 2.16 ppm with an integral ratio of 1:3 is observed. Whether the structure of **1** in solution corresponds to that in the solid state remains to be clarified. In contrast, the related Pt_2Ga_5 complex $[Pt_2(GaCp^*)_2(\mu_2\text{-}GaCp^*)_3]$ (**4**) exhibits non-fluxional behavior in solution.[10] Experiments to prepare mononuclear $[Pd(InCp^*)_4]$ (**2**) from **1** and excess of $[InCp^*]$ failed. Instead, the ^1H NMR spectrum of a mixture of **1** and $[InCp^*]$ (1:4) shows coalescence of the signals of **1** ($\delta = 2.12$ ppm) and $[InCp^*]$ ($\delta = 2.04$ ppm) at $\delta = 2.07$ ppm (calcd at $\delta = 2.09$ ppm). The product that crystallizes from this solution is pure **1**. In contrast, the monomeric M–Ga Complexes $[Pt(GaCp^*)_4]$ (**3a**) and $[Pd(GaCp^*)_4]$ (**3b**) (which are analogous to **2**) are readily available from $[Pt(cod)_2]$ (cod = *cis,cis*-1,5-cyclooctaiene) or $[(tmeda)Pd(CH_3)_2]$ and $[GaCp^*]$, respectively,[16] and thus complete the homologous series $[M(GaCp^*)_4]$ (M = Ni,[7a] Pd, Pt). Additionally, the dinuclear Pt complex $[Pt_2(GaCp^*)_2(\mu_2\text{-}GaCp^*)_3]$ (**4**), which is related to the title complex **1**, is also formed in the reaction of $[Pt(GaCp^*)_4]$ (**3a**) with $[Pt(cod)_2]$ and $[GaCp^*]$ in an exact molar ratio of 1:1:1 (Scheme 2). Treatment of **4** with $[GaCp^*]$ at 25 °C leads in a very slow, nonquantitative reaction back to **3a**. Likewise, **3a** is not available from $[Pt(\eta^2\text{-}C_2H_4)_3]$ and excess of $[GaCp^*]$: In this case **4** is exclusively formed. Clearly, complex mechanisms occur in which kinetic factors and association–dissociation equilibria play a key role. At least for the fluxional Pd/In system very similar lattice energies of the molecular crystals could be responsible for the preferred formation of **1** over **2** or alternative products even in presence of excess of $[InCp^*]$.[11]



Scheme 2. General scheme for the preparation of homoleptic Pt^0-[GaCp*] complexes. 1) Excess of [Cp*Ga], 2) $[Pt(cod)_2]$ and one equivalent of [Cp*Ga] in toluene.

Closer inspection of the synthesis of the title compound **1** (Scheme 1) reveals that the formation of $[Pd(PR_3)_4]$ from $[(tmeda)Pd(CH_3)_2]$ and phosphanes occurs by reductive elimination of ethane induced by precoordination of PR_3 and subsequent replacement of the tmeda ligand by PR_3.[17] Thus, the reaction of $[InCp^*]$ with $[(tmeda)Pd(CH_3)_2]$ in a ratio of 4:1 to give $[Pd(InCp^*)_4]$ (**2**) can be considered to have proceeded as expected. Similarly, the related syntheses of the PtE_2 complexes $[(dcpe)Pt(ER)_2]$[9] (E = Al, Ga, In; R = $C(SiMe_3)_3$, Cp*) from $[(dcpe)Pt(H)(CH_2\mathit{t}Bu)]$ and exactly two molar equivalents of ER in methylcyclohexane show a remarkable increase of the reaction rate (100% yield in 20–30 min at 70 °C)[18] in comparison to the unimolecular elimination of neopentane from $[(dcpe)Pt(H)(CH_2\mathit{t}Bu)]$ in the same solvent ($t_{1/2} = 2$ h at 70 °C).[19] In contrast, another pathway becomes more important in the reaction of $[(tmeda)Pd(CH_3)_2]$ with $[GaCp^*]$ and $[InCp^*]$: The reduction of Pd^{II} to Pd^0 is accompanied by the transfer of a methyl group to the Ga or In centers, that is, an oxidation giving a Ga^{III} or In^{III} side product, respectively (Scheme 1 and Scheme 3).[20] Monitoring of our reactions by NMR spectroscopy showed only traces of ethane. The classical reaction mechanisms of CO-containing complexes, that is, "insertion" into M–C(alkyl) bonds and "reductive elimination", can evidently be transferred to $[GaCp^*]$ and $[InCp^*]$ ligands. Experiments that used


$$a[Pd(tmeda)(CH_3)_2] + (a+b)[ECp^*] \xrightarrow{1)} [Pd_a(ECp^*)_b] + a[(CH_3)_2ECp^*]$$

3b (E = Ga)
1 (E = In)

Scheme 3. General scheme for the preparation of homoleptic Pd^0-[GaCp*] and Pd^0–[InCp*] complexes. For E = Ga, $a = 1$ and $b = 4$ (**3b**); for E = In, $a = 3$, and $b = 8$ (**1**).

[(tmeda)PdCl$_2$] as the precursor showed that a reduction of palladium(II) chlorides by [InCp*] and [GaCp*] leading to formation of [Cp*ECl$_2$] is in principle possible, but these reactions are less selective and yields are lower.

In summary, our results confirm the opening quotation that [InCp*] and [GaCp*] exhibit interesting potential as novel ligands for transition metals which exceeds the analogy to CO ligands and phosphanes. In this context, it is worth mentioning that photolysis of a solution of **1** in C_6D_6 (25 °C, 2 h, 150 W) results in selective cleavage of the Cp* shell of the Pd_3In_8 in the form of decamethylfulvalene, and we are currently investigating the metallic precipitate formed. The results are indicative of a link to the current field of mixed-metal nanoparticles and colloids.

Experimental Section

1: A solution of [(tmeda)Pd(CH$_3$)$_2$] (0.100 g, 0.396 mmol) in hexane (4 mL) was treated with four equivalents of [InCp*] (0.396 g, 1.584 mmol) in hexane (10 mL). The reaction mixture was warmed to 60 °C for 1 h, whereupon a red crystalline precipitate was formed. After recrystallization from benzene, the crystals were isolated by removal of the mother liquor by using a cannula, washed twice with a small amount of cold hexane, and dried in vacuo. Yield: 0.275 g, 90 %. M.p. 81 °C (decomp); ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 2.12$ ppm (s, 120 H); ^{13}C NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 113.7$, 11.2 ppm; elemental analysis: calcd for $C_{80}H_{120}In_8Pd_3\cdot C_6D_6$: C 42.97; H 5.53, found: 42.79, 5.64.

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[1] R. Murugavel, V. Chandrasekhar, *Angew. Chem.* **1999**, *111*, 1289–1293; *Angew. Chem. Int. Ed.* **1999**, *38*, 1211–1215.

[2] a) W. Uhl, M. Pohlmann, R. Wartchow, *Angew. Chem.* **1998**, *110*, 1007–1009; *Angew. Chem. Int. Ed.* **1998**, *37*, 961–963; b) W. Uhl, S. Melle, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2043–2045; c) W. Uhl, M. Benter, S. Melle, W. Saak, G. Frenking, J. Uddin, *Organometallics* **1999**, *18*, 3778–3780.

[3] P. Jutzi, B. Neumann, L. O. Schebaum, A. Stammler, H. G. Stammler, *Organometallics* **1999**, *18*, 4462–4464.

[4] J. Weiss, D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme, G. Frenking, *Angew. Chem.* **1997**, *109*, 95–97; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 70–72.

[5] a) P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1998**, *17*, 1305–1314; b) W. Uhl, M. Pohlmann, *Organometallics* **1997**, *16*, 2478–2480, and references therein.

[6] J. Uddin, G. Frenking, *J. Am. Chem. Soc.* **2001**, *123*, 1683–1693.

[7] a) P. Jutzi, B. Neumann, L. O. Schebaum, A. Stammler, H. G. Stammler, *Organometallics* **1999**, *18*, 4462–4464; b) E. V. Grachova, P. Jutzi, B. Neumann, L. O. Schebaum, H. G. Stammler, S. P. Tunik, *J. Chem. Soc. Dalton Trans.* **2002**, 302–304.

[8] C. Dohmeier, H. Krautscheid, H.-G. Schnöckel, *Angew. Chem.* **1994**, *106*, 2570–2571; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2482–2483.

[9] a) D. Weiss, T. Steinke, M. Winter, R. A. Fischer, *Organometallics* **2000**, *19*, 4583–4588; b) D. Weiss, M. Winter, K. Merz, A. Knüfer, R. A. Fischer, *Polyhedron* **2002**, *21*, 535–542.

[10] D. Weiss, M. Winter, R. A. Fischer, C. Yu, K. Wichmann, G. Frenking, *Chem. Commun.* **2000**, 2495–2496.

[11] Crystal structure analysis of $\mathbf{1}\cdot C_6D_6$: crystal size: 0.35 × 0.28 × 0.20 mm, triclinic, $P\bar{1}$, $a = 12.826(3)$, $b = 16.146(4)$, $c = 25.215(6)$ Å, $\alpha = 97.595(4)$, $\beta = 101.316(4)$, $\gamma = 111.313(4)°$, $V = 4650.0(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.657$ mg m^{-3}, $2\Theta_{max.} = 50.160$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 213(3)$ K. A total of 23 924 reflections (16 005 unique) were collected on a Bruker-axs SMART diffractometer (R(int) = 0.0322). The structure solution and refinement was performed by using the programs SHELXS-86 and SHELXL-97. The final values for $R1$ and $wR2(F^2)$ were 0.0705 and 0.2253, respectively. The reason for the unusually high value for $wR2(F^2)$ is not yet clear and is currently under investigation. The Cp* rings at In2 and In8 were isotropically refined and the interatomic distances and angles in all of the Cp* rings were fixed. The Cp* rings are disordered. The unit cell contains other atoms, which probably belong to benzene molecules, but cannot be accurately assigned and refined. As the molecular structure of **1** clearly shows, the high steric demand of the Cp* units excludes the formation of higher [Pd(InCp*)$_2$] oligomers. The key for the synthesis of [Pd(InCp*)$_2$]$_n$ ($n > 3$) is the design of new, sterically less hindered, yet soluble ligands of the type In(CpR) (R = alkyl). CCDC-187560 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] U. Häussermann, M. Elding-Pontén, C. Svensson, S. Lidin, *Chem. Eur. J.* **1998**, *4*, 1007–1015.

[13] R. D. Feltham, G. Elbaze, R. Ortega, C. Eck, J. Dubrawski, *Inorg. Chem.* **1985**, *24*, 1503–1510.

[14] O. T. Beachley, Jr., A. Blom, M. R. Churchill, K. Faegri, Jr., J. C. Fettinger, J. C. Pazik, L. Victoriano, *Organometallics* **1989**, *8*, 346–356.

[15] O. T. Beachley, Jr., M. R. Churchill, J. C. Fettinger, J. C. Pazik, L. Victoriano, *J. Am. Chem. Soc.* **1986**, *108*, 4666–4668.

[16] T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, unpublished results, **2002**.

[17] a) W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1989**, *8*, 2907–2917; b) J. Krause, G. Cestaric, K.-J. Haack, K. Seevogel, W. Storm, K.-R. Pörschke, *J. Am. Chem. Soc.* **1999**, *121*, 9807–9823.

[18] D. Weiss, Ph.D. thesis, Ruhr-Universität Bochum, **2001**.

[19] a) M. Hackett, G. M. Whitesides, *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448; b) M. Hackett, G. M. Whitesides, *J. Am. Chem. Soc.* **1988**, *110*, 1449–1462.

[20] Identification of the Ga^{III} and In^{III} side products by ^{1}H and ^{13}C NMR spectroscopy (C_6D_6, 250 MHz, 25 °C). [Cp*Ga(CH$_3$)$_2$]: ^{1}H NMR: $\delta = -0.15$ ppm; ^{13}C NMR: $\delta = -7.8$ ppm. [Cp*In(CH$_3$)$_2$]: ^{1}H NMR: $\delta = -0.11$ ppm; ^{13}C NMR: $\delta = -6.9$ ppm.

Total Synthesis of Amphidinolide T4**

Alois Fürstner,* Christophe Aïssa, Ricardo Riveiros, and Jacques Ragot

Marine dinoflagellates of the genus *Amphidinium* sp. living in symbiosis with the Okinawan (Japanese) flatworm *Amphiscolops* sp. are exceedingly rich sources of bioactive macrolides.[1] Though structurally quite diverse, all "amphidinolides" known to date exhibit pronounced cytotoxicity against various cancer cell lines, with some members reaching potencies which rank them amongst the most cytotoxic compounds that are presently known.[2] In contrast to macrolide antibiotics derived from terrestrial microorganisms, the majority of amphidinolides feature an odd-numbered macrolide ring, which raises questions concerning the biosynthesis of these structurally unique secondary metabolites.

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