Polycyclic Aromatics

DOI: 10.1002/ange.201403245

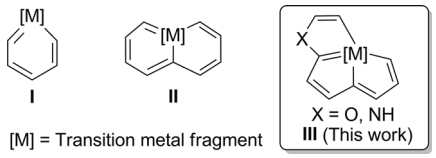
A Metal-Bridged Tricyclic Aromatic System: Synthesis of Osmium Polycyclic Aromatic Complexes**

Congqing Zhu, Qin Zhu, Jinglan Fan, Jun Zhu, Xumin He, Xiao-Yu Cao, and Haiping Xia**

Abstract: *Aromaticity is one of the most important concepts in organic chemistry. A variety of metalla-aromatic compounds have been recently prepared and in most of those examples, the metal participates only in a monocyclic ring. In contrast, metal-bridged bicyclic aromatic molecules, in which a metal is shared between two aromatic rings, have been less developed. Herein, we report the first metal-bridged tricyclic aromatic system, in which the metal center is shared by three aromatic five-membered rings. These metalla-aromatics are formed by reaction between osmapentalyne and arene nucleophiles. Experimental results and theoretical calculations reveal that the three five-membered rings around the osmium center are aromatic. In addition, the broad absorption bands in the UV/Vis absorption spectra of these novel aromatic systems cover almost the entire visible region. This straightforward synthetic strategy may be extended to the synthesis of other metal-bridged polycyclic aromatics.*

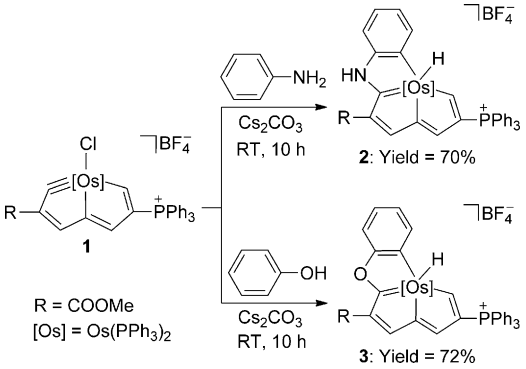
Aromaticity is a fascinating topic in chemistry and continues to attract attention.[1] Metalla-aromatic molecules, first proposed by Thorn and Hoffmann in 1979, are analogues of conventional aromatic molecules, in which one carbon segment is formally replaced by a transition-metal fragment.[2] Many metalla-aromatics have been synthesized since that time.[3] Most of the well-characterized metalla-aromatic systems contain five- or six-membered rings with the characteristic feature that the metal participates only in one ring system (type **I**, Scheme 1).[4–7] In contrast, the metal-bridged bicyclic aromatics, which contain a metal that is shared by two aromatic rings (type **II**, Scheme 1), have been less developed.[7g,8]

Metal-bridged bicyclic aromatics are interesting because the bridge-head metal can stabilize and influence both rings, thus creating metalla-aromaticity in an extended, π-electron conjugated framework.[8g,h] In addition, the coordination number of a bridge-head transition-metal atom is larger than that of a bridge-head carbon atom, and bridge-head transition-metal atoms can form planar, polycyclic aromatic systems. Herein, we report the synthesis, structural characterization, spectroscopic properties, and density functional theory (DFT) calculations of the metal-bridged tricyclic aromatic system (type **III**, Scheme 1), in which the metal center is shared by three aromatic five-membered rings.



Scheme 1. Classes of metalla-aromatic molecules: metal non-bridged aromatics (**I**), metal-bridged bicyclic aromatics (**II**), and metal-bridged tricyclic aromatics (**III**).

The synthetic routes for tricyclic aromatics **2** and **3** are shown in Scheme 2. The treatment of osmapentalyne **1**[8g] with aniline at room-temperature (RT) in the presence of Cs_2CO_3 provided complex **2** in 70% yield. This reaction proceeds by the nucleophilic addition of osmapentalyne **1** to the carbyne, followed by C–H bond activation to form complex **2**. A detailed mechanism for the formation of **2** is proposed in Scheme S1 in the Supporting Information. Complex **2** is stable in the solid state, even upon heating at 150 °C in air for 3 h. Under the same conditions, osmapentalyne **1** reacted with phenol to produce complex **3** which was isolated in 72% yield.



Scheme 2. Syntheses of polycyclic metalla-aromatic compounds **2** and **3**.

The structure of complex **2** was determined by single-crystal X-ray diffraction.[9] The unit cell contains two independent molecules with similar structural features. One of the molecules is shown in Figure 1. The osmium center in

[*] C. Zhu, Q. Zhu, J. Fan, Dr. J. Zhu, Prof. Dr. X. He, Dr. X.-Y. Cao, Prof. Dr. H. Xia
State Key Laboratory of Physical Chemistry of Solid Surfaces and Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), and Department of Chemistry, Xiamen University
Xiamen 361005 (China)
E-mail: xcao@xmu.edu.cn
hpxia@xmu.edu.cn
Homepage: http://chem.xmu.edu.cn/group/hpxia/index.htm

[**] We thank the 973 Program (2012CB821600), the NSFC (Nos. 21332002 and 21102120), and the program for Changjiang Scholars and Innovative Research Team in University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201403245.

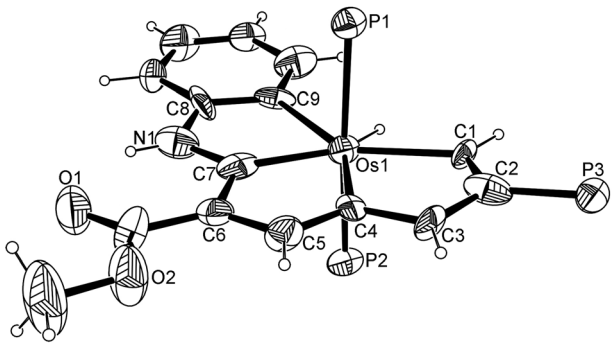
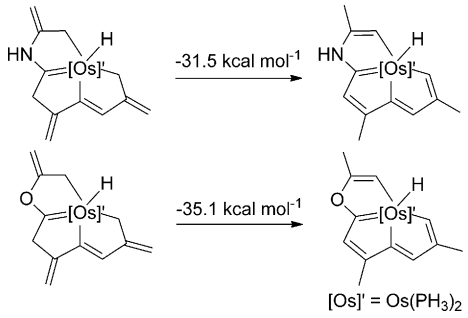


Figure 1. Molecular structure of the cation of **2** (thermal ellipsoids set at 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1-C1 2.175(8), Os1-C4 2.083(10), Os1-C7 1.999(12), Os1-C9 2.151(9), C1-C2 1.347(14), C2-C3 1.389(15), C3-C4 1.450(12), C4-C5 1.369(14), C5-C6 1.390(13), C6-C7 1.457(15), C7-N1 1.400(12), N1-C8 1.427(14), C8-C9 1.371(15); Os1-C1-C2 116.6(8), C1-C2-C3 118.6(11), C2-C3-C4 110.9(9), C3-C4-Os1 120.0(7), C4-Os1-C1 73.8(4), Os1-C4-C5 122.2(7), C4-C5-C6 113.0(10), C5-C6-C7 108.8(10), C6-C7-Os1 123.8(7), C7-Os1-C4 71.9(4), Os1-C7-N1 123.0(9), C7-N1-C8 110.8(10), N1-C8-C9 115.4(10), C8-C9-Os1 116.1(8), C9-Os1-C7 74.5(4).

complex **2** is seven-coordinate with an approximately pentagonal bipyramidal coordination geometry. The metal center is shared by three fused five-membered rings. These rings (composed of Os1, N1, and C1–C9) are almost coplanar, as reflected by the small mean deviation from the least-squares plane (0.0422 Å). The sums of angles in the three five-membered rings are 539.9°, 539.7°, and 539.8°, which are in close agreement with the ideal value of 540°. Interestingly, four carbon atoms surround the metal center in the equatorial plane. All Os–C bond lengths in **2** (1.999–2.175 Å) are within the typical range of Os–C single- and double-bond lengths.[10]

Complexes **2** and **3** were further characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS). In the ^{1}H NMR spectrum of complex **2**, the resonance in the upfield region ($\delta = -3.51$ ppm) can be assigned to the OsH, the signal at $\delta = 11.26$ ppm to the NH, and the signal at $\delta = 11.63$ ppm to the OsCH, which falls in the expected range of OsCH proton resonances in osmapentalenes ($\delta = 11.93$–12.46 ppm).[8h] The remaining two proton signals attributable to the fused five-membered rings of **2** lie in the aromatic region (H3: $\delta = 8.19$ ppm, H5: $\delta = 9.06$ ppm). The molecular ion in the HRMS of **2** was observed at *m*/*z* 1216.3214, in agreement with the calculated value (*m*/*z* 1216.3211). The NMR spectra of **3** are similar to those of **2** (Supporting Information).

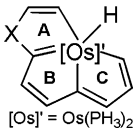
The aromaticity of complexes **2** and **3** was suggested by their planarity, their high stability, and the characteristic downfield chemical shifts of the peaks in their ^{1}H NMR spectra. To verify the aromaticity of complexes **2** and **3**, we calculated the isomerization stabilization energy values (ISE)[11] based on simplified unsubstituted models **2′** and **3′** (by replacement of the PPh_3 ligands with PH_3 groups). The ISE values of **2′** and **3′** are −31.5 and −35.1 kcal mol^{-1} (Scheme 3); these values are close to those of aromatic osmapentalenes (−25.7 and −30.7 kcal mol^{-1}) evaluated by the same method.[8h]



Scheme 3. The aromaticity of **2′** and **3′** evaluated by the ISE method. The energies include zero-point energy corrections.

To further evaluate the aromatic character of this novel metal-bridged tricyclic aromatic system, we calculated the nucleus-independent chemical shift values (NICS)[12] for **2′** and **3′**. In general, negative NICS values indicate aromaticity and positive values suggest anti-aromaticity. The calculated NICS(1) values are −6.3, −7.5, and −11.2 ppm for the three five-membered rings of model **2′**; when the environments at the points 1 Å above and below the ring centers were not equivalent, the averaged values were used for NICS(1) and NICS(1)$_{zz}$ (Table 1). These NICS(1) values are comparable to

Table 1: NICS(1) and NICS(1)$_{zz}$ values (in ppm) at rings **A**, **B**, and **C** of **2′** and **3′** calculated at the B3LYP/6-311++G(d,p) level.

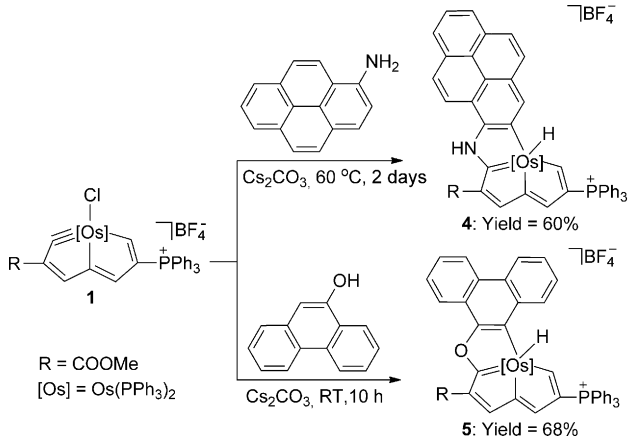


Ring	NICS(1)		NICS(1)$_{zz}$	
	2′; X = NH	**3′**; X = O	**2′**; X = NH	**3′**; X = O
A	−6.3	−6.5	−10.7	−9.1
B	−7.5	−8.4	−14.1	−16.8
C	−11.2	−11.8	−23.9	−25.5

those of benzene (−10.2 ppm)[8g] and osmapentalynes (ranging from −11.6 to −8.0 ppm).[8g] The NICS(1) values of the three five-membered rings of **3′** are also negative (−6.5, −8.4, and −11.8 ppm). The NICS(1)$_{zz}$ values (the tensor z-component of NICS(1)) of each ring in **2′** and **3′** are even more negative (Table 1). The ISE and NICS calculations suggest that complexes **2** and **3** have a unique metal-bridged tricyclic aromatic core in which the metal center is shared by three aromatic five-membered rings.

To extend the scope of the reaction of arene nucleophiles with metallapentalyne and to prepare larger metalla-aromatic systems, we treated osmapentalyne **1** with commercially available 1-aminopyrene as a proof-of-concept test. Metal-bridged polycyclic complex **4** was isolated in 60% yield after the reaction mixture was heated under reflux at 60 °C in the presence of Cs_2CO_3 for 2 days (Scheme 4). Complex **5** was obtained by the reaction of osmapentalyne **1** with 9-phenanthrenol at room temperature.

Complex **4** was characterized by NMR spectroscopy, HRMS, and X-ray crystallographic analysis. In the ^{1}H NMR



Scheme 4. Preparation of metalla-aromatic compounds **4** and **5**.

spectrum, the characteristic signals of OsH and NH appear at $\delta = -2.90$ and 12.49 ppm, whereas the signals of H1, H3, and H5 appear at $\delta = 11.96$, 8.48, and 9.28 ppm, respectively. Complex **5** was also characterized by NMR spectroscopy and HRMS (Supporting Information).

The single-crystal X-ray structure of **4** clearly indicates that the coordination mode of osmium is similar to that in complex **2**. As shown in Figure 2, the geometry of the metal

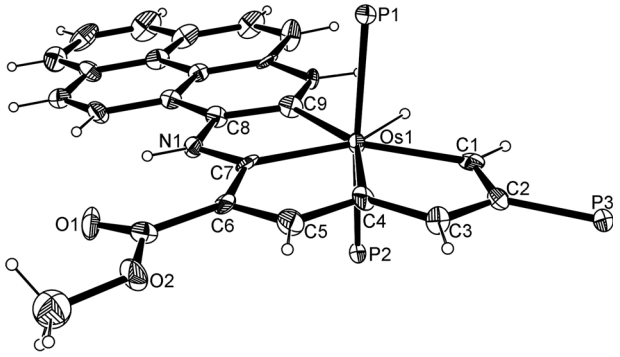


Figure 2. Molecular structure of the cation of **4** (thermal ellipsoids set at 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1-C1 2.084(5), Os1-C4 2.127(5), Os1-C7 2.048(5), Os1-C9 2.156(5), C1-C2 1.362(6), C2-C3 1.410(7), C3-C4 1.370(7), C4-C5 1.426(7), C5-C6 1.386(7), C6-C7 1.451(7), C7-N1 1.337(6), N1-C8 1.397(6), C8-C9 1.415(7); Os1-C1-C2 120.3(4), C1-C2-C3 114.5(5), C2-C3-C4 112.8(4), C3-C4-Os1 119.3(4), C4-Os1-C1 73.05(19), Os1-C4-C5 118.9(4), C4-C5-C6 113.9(5), C5-C6-C7 111.6(5), C6-C7-Os1 122.0(4), C7-Os1-C4 73.5(2), Os1-C7-N1 120.9(4), C7-N1-C8 116.0(4), N1-C8-C9 113.3(4), C8-C9-Os1 115.3(3), C9-Os1-C7 74.46(19).

center approximates a pentagonal bipyramid and the osmium is shared between three five-membered rings. The sums of angles in the three five-membered rings are 540.0°, 539.9°, and 540.0°, which are in good agreement with the ideal value of 540°. The Os1−C1 (2.084 Å), Os1−C4 (2.127 Å) and Os1−C7 (2.048 Å) distances are within the range of the Os–C bond lengths observed in osmapentalene (1.926–2.139 Å), whereas the Os1−C9 distance (2.156 Å) is slightly longer.[8h] The carbon–carbon bonds (1.362–1.451 Å) in the fused five-membered rings fall within the range of carbon–carbon single- and double-bonds.

The UV/Vis absorption spectra of these unusual metal-bridged polycyclic aromatics **2**–**5** are summarized in Figure 3. In the visible region, the absorption maximum of **2** is $\lambda = 528$ nm (log $\varepsilon = 3.81$, ε: molar extinction coefficient in $M^{-1}cm^{-1}$), and the absorption maximum of **3** is $\lambda = 461$ nm

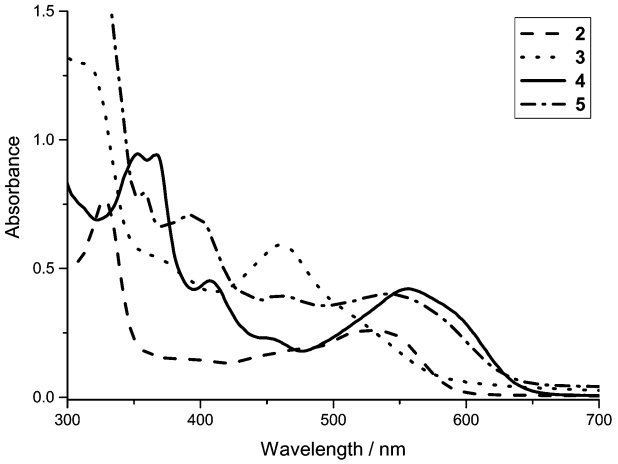


Figure 3. UV/Vis absorption spectra of **2**–**5** measured in CH_2Cl_2 at room temperature.

(log $\varepsilon = 3.75$). Upon increasing the size of the aromatic framework, the absorption maximum of complex **4** in the visible region ($\lambda_{max} = 557$ nm, log $\varepsilon = 4.06$) is red-shifted by 29 nm compared with that of **2**. Complex **5** also has an absorption maximum ($\lambda_{max} = 541$ nm, log $\varepsilon = 3.56$) that is red-shifted by 80 nm from that of **3**. This suggests that the effective conjugation lengths of both **4** and **5** are longer than those of their simpler analogues.

To understand the absorption spectra, we performed time-dependent density functional theory (TD-DFT) calculations on the simplified model **4**′′ (where the PPh_3 groups in **4** were replaced with PH_3 groups) at the B3LYP/6-311++G(d,p) level. We first optimized the geometry of **4**′′ (Figure S1 in the Supporting Information). This was found to be consistent with the X-ray structure. The HOMO was mainly localized on the pyrene moiety, whereas the LUMO was mostly localized on the metal-bridged fused five-membered rings (Figure 4). The calculated absorption bands of **4**′′ at $\lambda = 574$, 428, 388, and 359 nm are consistent with the bands observed at $\lambda = 557$, 407, 367, and 353 nm of complex **4**, respectively. These computed absorption bands can be assigned to the electronic transitions HOMO→LUMO, HOMO→LUMO+1, HOMO−2→LUMO, and HOMO→LUMO+2, respectively (Supporting Information).

In summary, we have prepared and characterized a series of novel metal-bridged polycyclic aromatic systems derived from osmapentalyne and arene nucleophiles. The planarity, high stability, downfield proton chemical shifts, and calculated ISE and NICS values confirmed the aromaticity of these complexes. In a preliminary test, this straightforward and

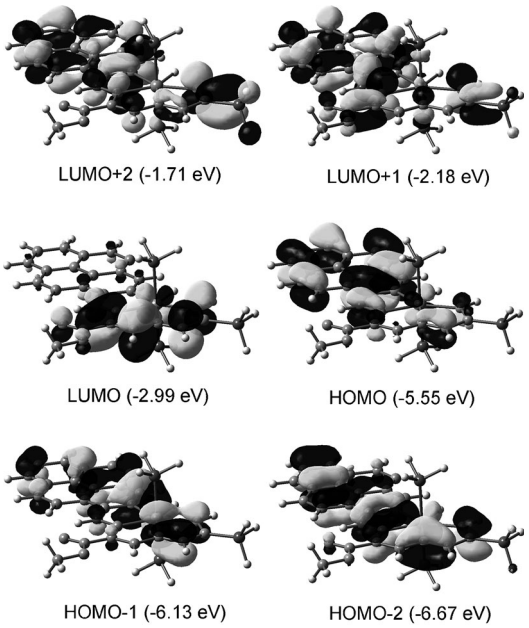


Figure 4. Molecular orbitals of **4″** based on calculations at the B3LYP/6-311++G(d,p) level. The eigenvalues of the molecular orbitals are given in parentheses.

versatile synthetic strategy provided planar metalla-aromatic complexes containing up to seven fused aromatic rings, thus providing possibilities for the preparation of a novel family of large polycyclic metalla-aromatics or even metalla-nanographene.

Received: March 12, 2014
Published online: April 29, 2014

Keywords: aromaticity · density functional calculations · metal carbyne · metallapentalyne · osmium

[1] a) V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity*, Wiley, New York, **1994**; b) special issue on aromaticity: *Chem. Rev.* **2001**, *101*, 1115; c) special issue on delocalization: *Chem. Rev.* **2005**, *105*, 3433; d) H. Ottosson, *Nat. Chem.* **2012**, *4*, 969.

[2] D. L. Thorn, R. Hoffman, *Nouv. J. Chim.* **1979**, *3*, 39.

[3] For Reviews see: a) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205; b) G. Jia, *Acc. Chem. Res.* **2004**, *37*, 479; c) C. W. Landorf, M. M. Haley, *Angew. Chem.* **2006**, *118*, 4018; *Angew. Chem. Int. Ed.* **2006**, *45*, 3914; d) L. J. Wright, *Dalton Trans.* **2006**, 1821; e) J. R. Bleeke, *Acc. Chem. Res.* **2007**, *40*, 1035; f) G. Jia, *Coord. Chem. Rev.* **2007**, *251*, 2167; g) M. Paneque, M. L. Poveda, N. Rendón, *Eur. J. Inorg. Chem.* **2011**, 19; h) J. Chen, G. Jia, *Coord. Chem. Rev.* **2013**, *257*, 2491; i) X.-Y. Cao, Q. Zhao, Z. Lin, H. Xia, *Acc. Chem. Res.* **2014**, *47*, 341; j) B. J. Frogley, L. J. Wright, *Coord. Chem. Rev.* **2014**, *270*, 151.

[4] Examples of metallabenzenes: a) G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811; b) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem.* **2002**, *114*, 3620; *Angew. Chem. Int. Ed.* **2002**, *41*, 3470; c) H. Xia, G. He, H. Zhang, T. B. Wen, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 6862; d) H. Zhang, H. Xia, G. He, T. B. Wen, L. Gong, G. Jia, *Angew. Chem.* **2006**, *118*, 2986; *Angew. Chem. Int. Ed.* **2006**, *45*, 2920; e) E. Álvarez, M. Paneque, M. L. Poveda, N. Rendón, *Angew. Chem.* **2006**, *118*, 488; *Angew. Chem. Int. Ed.* **2006**, *45*, 474; f) V. Jacob, C. W. Landorf, L. N. Zakharov, T. J. R. Weakley, M. M. Haley, *Organometallics* **2009**, *28*, 5183; g) K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2010**, *122*, 2819; *Angew. Chem. Int. Ed.* **2010**, *49*, 2759; h) J. Chen, C. Zhang, T. Xie, T. Wen, H. Zhang, H. Xia, *Organometallics* **2013**, *32*, 3993; i) Á. Vivancos, M. Paneque, M. L. Poveda, E. Álvarez, *Angew. Chem.* **2013**, *125*, 10252; *Angew. Chem. Int. Ed.* **2013**, *52*, 10068; j) C. Huang, Y. Hao, Y. Zhao, J. Zhu, *Organometallics* **2014**, *33*, 817.

[5] Examples of metallabenzynes: a) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem.* **2001**, *113*, 2005; *Angew. Chem. Int. Ed.* **2001**, *40*, 1951; b) T. B. Wen, S. M. Ng, W. Y. Hung, Z. Y. Zhou, M. F. Lo, L.-Y. Shek, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2003**, *125*, 884; c) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856; d) W. Y. Hung, J. Zhu, T. B. Wen, K. P. Yu, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2006**, *128*, 13742; e) J. Chen, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2011**, *123*, 10863; *Angew. Chem. Int. Ed.* **2011**, *50*, 10675; f) W. Y. Hung, B. Liu, W. Shou, T. B. Wen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2011**, *133*, 18350; g) J. Fan, K. An, X. Wang, J. Zhu, *Organometallics* **2013**, *32*, 6271.

[6] Examples of other monocyclic metalla-aromatics: a) J. R. Bleeke, M. F. Ortwerth, M. Y. Chiang, *Organometallics* **1993**, *12*, 985; b) J. R. Bleeke, J. M. B. Blanchard, *J. Am. Chem. Soc.* **1997**, *119*, 5443; c) J. R. Bleeke, P. V. Hinkle, N. P. Rath, *J. Am. Chem. Soc.* **1999**, *121*, 595; d) F. M. Alías, P. J. Daff, M. Paneque, M. L. Poveda, E. Carmona, P. J. Pérez, V. Salazar, Y. Alvarado, R. Atencio, R. Sánchez-Delgado, *Chem. Eur. J.* **2002**, *8*, 5132; e) B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem.* **2009**, *121*, 5538; *Angew. Chem. Int. Ed.* **2009**, *48*, 5430.

[7] Examples of metal non-bridged polycyclic aromatics: a) J. Yang, W. M. Jones, J. K. Dixon, N. T. Allison, *J. Am. Chem. Soc.* **1995**, *117*, 9776; b) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898; c) G. He, J. Zhu, W. Y. Hung, T. B. Wen, H. H.-Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2007**, *119*, 9223; *Angew. Chem. Int. Ed.* **2007**, *46*, 9065; d) M. A. Esteruelas, A. B. Masamunt, M. Oliván, E. Oñate, M. Valencia, *J. Am. Chem. Soc.* **2008**, *130*, 11612; e) J. R. Bleeke, P. Putprasert, T. Thananatthanachon, *Organometallics* **2008**, *27*, 5744; f) B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem.* **2009**, *121*, 5569; *Angew. Chem. Int. Ed.* **2009**, *48*, 5461; g) T. Wang, S. Li, H. Zhang, R. Lin, F. Han, Y. Lin, T. B. Wen, H. Xia, *Angew. Chem.* **2009**, *121*, 6575; *Angew. Chem. Int. Ed.* **2009**, *48*, 6453.

[8] Examples of metalla-aromatics in which the metal is shared by two aromatic rings: a) T. Wang, H. Zhang, F. Han, R. Lin, Z. Lin, H. Xia, *Angew. Chem.* **2012**, *124*, 9976; *Angew. Chem. Int. Ed.* **2012**, *51*, 9838; b) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771; c) G. R. Clark, T. R. O'Neale, W. R. Roper, D. M. Tonei, L. J. Wright, *Organometallics* **2009**, *28*, 567; d) G. R. Clark, P. M. Johns, W. R. Roper, T. Söhnel, L. J. Wright, *Organometallics* **2011**, *30*, 129; e) G. R. Clark, G.-L. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167; f) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536; g) C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. Wen, Z. Xie, P. v. R. Schleyer, H. Xia, *Nat. Chem.* **2013**, *5*, 698; h) C. Zhu, M. Luo, Q. Zhu, J. Zhu, P. v. R. Schleyer, J. I.-C. Wu, X. Lu, H. Xia, *Nat. Commun.* **2014**, *5*, 3265; i) X. Wang, C. Zhu, H. Xia, J. Zhu, *Organometallics* **2014**, *33*, 1845.

[9] CCDC 982358 (**2**) and 982359 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained

free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

[10] Based on a search of the Cambridge Structural Database, CSD version 5.34 (May **2013**).

[11] a) P. v. R. Schleyer, F. Pühlhofer, *Org. Lett.* **2002**, *4*, 2873; b) J. Zhu, K. An, P. v. R. Schleyer, *Org. Lett.* **2013**, *15*, 2442.

[12] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) Z. F. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842; c) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863.