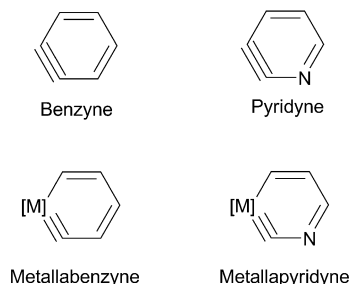


Synthesis and Characterization of a Metallapyridyne Complex**

Tongdao Wang, Hong Zhang, Feifei Han, Ran Lin, Zhenyang Lin,* and Haiping Xia*

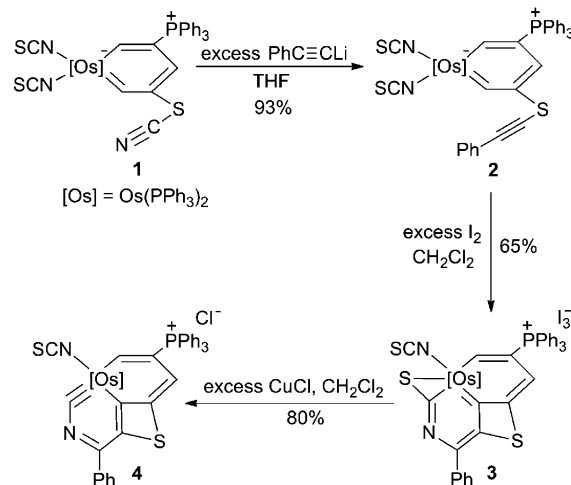
Arynes are generally considered as useful reactive intermediates because they can participate in a wide variety of chemical transformations.^[1–3] As a model compound of arynes, benzyne has been extensively investigated.^[2] Pyridyne, a heterocyclic



counterpart of benzyne, has also been extensively studied using numerous trapping methodologies.^[3]

As new aromatic heterocycles, metallaaromatics are currently attracting attention because of their aromatic properties and organometallic reactivities.^[4,5] The existence of metallabenzynes, which are organometallic compounds derived from formal replacement of an alkyne carbon atom in benzyne with an isolobal transition-metal fragment, has been proven by Jia and co-workers in recent years.^[6] The discovery of metallabenzynes raised the interesting questions of whether metallapyridynes exist and of how they could be made available for chemical manipulation. In principle, replacement of an alkyne carbon atom in pyridynes with an isolobal transition-metal fragment would result in metallapyridynes. Herein, we report the preparation and structural characterization of the first metallapyridyne complex.

Scheme 1 illustrates the synthetic route to the polycyclic osmium complexes. Treatment of **1** with excess $\text{PhC}\equiv\text{CLi}$ in tetrahydrofuran at 0 °C led to the formation of the osmabenzene **2**. Complex **2** was characterized by NMR spectroscopy and elemental analysis, and the structure was further con-



Scheme 1. Preparation of polycyclic osmium complexes **3** and **4**.

firmed by single-crystal X-ray diffraction.^[7] The structural data indicate that the metallacycle of **2** has a delocalized structure. Complex **2** is air stable both in the solid state and in solution. When treated with I_2 (4 equiv) in dichloromethane **2** was consumed completely, as indicated by in situ NMR spectroscopy, within twelve hours to give complex **3** as the major product (Scheme 1).

A pure sample of complex **3** can be obtained in 65 % yield from the reaction mixture after column chromatography. The structure of **3** was confirmed unambiguously by X-ray diffraction.^[7] As shown in Figure 1, complex **3** contains an essentially planar polycyclic metallacycle unit. The mean deviation from the least-squares plane through Os1, N1, and C1–C8 is 0.0193 Å, and the maximum deviation from the least-squares plane through all ten atoms is 0.0385 Å for C6. It is interesting that even the twelve atoms (Os1, N1, C1–C8, S1, S2) of the four rings are approximately coplanar, which is reflected by the mean deviation (0.0178 Å) from the least-squares plane. The metallapyridine ring of **3** is structurally related to the metallabenzene ring in the first metallabenzene reported by Roper and co-workers.^[8] Both complexes contain a sulfur-tethered metallaaromatic ring. As a result of the S2 atom competing for bonding with the metal center, the C8 atom, which is directly bonded to S2, has a weak bonding interaction with the metal center. The Os1–C8 bond (2.199(7) Å) is markedly longer than that of the Os1–C1 (2.065(8) Å) and Os1–C5 (1.996(7) Å) bonds. Compared with complex **2**, complex **3** shows considerable bond distance alternation within the metallacycles (C1–C2 1.333(10), C2–C3 1.451(10), C3–C4 1.363(10), C4–C5 1.458(10), C5–C6 1.435(10), C6–C7 1.352(11), C7–N1 1.411(10), N1–C8 1.230(9) Å). Nevertheless, the C–C and C–N bond

[*] T. Wang,^[†] Dr. H. Zhang,^[†] F. Han, Dr. R. Lin, Prof. Dr. H. Xia
Department of Chemistry, College of Chemistry and Chemical
Engineering, and State Key Laboratory of Physical Chemistry of Solid
Surfaces, Xiamen University, Xiamen, 361005 (China)
E-mail: hpxia@xmu.edu.cn

Dr. H. Zhang,^[†] Prof. Dr. Z. Lin
Department of Chemistry, The Hong Kong University of Science and
Technology, Clear Water Bay, Kowloon (Hong Kong)
E-mail: chzlin@ust.hk

[†] These authors contributed equally to this work.

[**] We thank the National Natural Science Foundation of China (Nos.
20801046 20925208) and the Fundamental Research Funds for the
Central Universities (No. 201112G002) and the 973 Program (No.
2012CB821600).

Supporting information for this article is available on the WWW
under <http://dx.doi.org/10.1002/anie.201204073>.

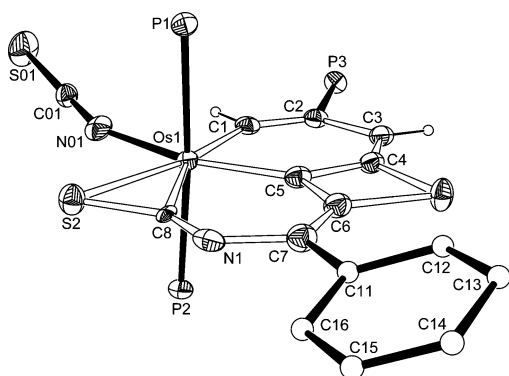
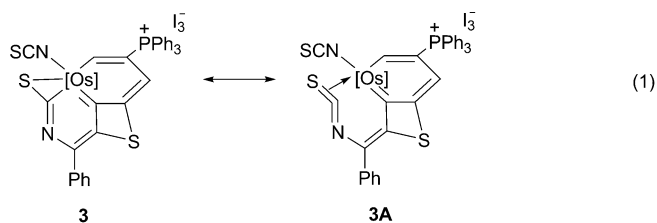


Figure 1. X-ray structure of complex **3**. Ellipsoids shown at the 50% probability level. Phenyl rings in PPh₃ groups, some of the hydrogen atoms and the counter anion are omitted for clarity. Selected bond distances [Å] and angles [°]: Os1–C1 2.065(8), Os1–C5 1.996(7), Os1–C8 2.199(7), Os1–S2 2.477(2), C1–C2 1.333(10), C2–C3 1.451(10), C3–C4 1.363(10), C4–C5 1.458(10), C4–S1 1.802(8), C6–S1 1.796(8), C5–C6 1.435(10), C6–C7 1.352(11), C7–N1 1.411(10), C8–N1 1.230(9), C8–S2 1.609(7); C5–Os1–C1 80.8(3), C8–Os1–C5 75.9(3), C8–Os1–S2 39.69(18), Os1–C1–C2 138.8(6), C1–C2–C3 122.7(7), C2–C3–C4 116.7(7), C3–C4–C5 130.1(7), C4–C5–Os1 130.9(6), C6–S1–C4 72.3(4), C6–C5–C4 94.3(6), C5–C4–S1 96.1(5), C5–C6–S1 97.2(5), C6–C5–Os1 134.7(6), C7–C6–C5 129.2(7), C6–C7–N1 115.9(7), C8–N1–C7 124.9(7), N1–C8–Os1 139.2(6), C8–S2–Os1 60.8(3), S2–C8–Os1 79.5(3).

distances are close to those found in other metallaromatic systems.^[5] It should be pointed out here that a similar bond distance alternation has also been observed in other metallabenzene systems containing either an SME,^[9] OH,^[6c] or OMe substituent.^[6e] Alternatively, one might consider **3A** [Eq. (1)], in which the complex is described as a π -bound

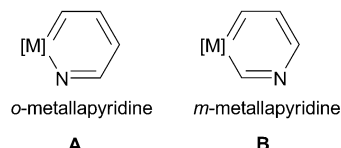


organoisothiocyanate, as a possible resonance form that contributes to the overall structure to account for the relatively short C8–S2 bond (1.609(7) Å). Therefore, the molecular structure is better described by a resonance hybrid of **3** and **3A** shown in Equation (1).

The closely related parent organic molecules of **3** are 1,8-thianaphthalene, which was determined by X-ray diffraction previously, and other single-atom peribridged naphthalenes (SAPN).^[10] As revealed by X-ray diffraction the C–S–C angle of **3** is 72.3(4)°, which is smaller than the corresponding angle in 1,8-thianaphthalene (73.06°),^[10] and it is the smallest bridging angle yet recorded for a SAPN derivative. It has been established that the smaller bridging angle could impose less strain on the aromatic moiety.^[10,11] We speculated that the small bridging angle may play an important role in the stability of complex **3**.

Consistent with the solid-state structure, the ¹H and ¹³C NMR chemical shifts of the ring atoms in complex **3** appear in the aromatic region. The ¹H NMR spectrum displayed the signal for OsCH at δ = 12.5 ppm and that for OsCHC(PPh₃)CH at δ = 7.3 ppm (determined by ¹H–¹³C HSQC). The ¹³C{¹H} NMR spectrum showed the eight signals corresponding to the eight carbon atoms of the metallacycle at δ = 202.5 (C1), 108.8 (C2), 127.6 (C3), 136.1 (C4), 222.2 (C5), 124.2 (C6), 146.8 (C7), and 198.6 (C8) ppm. The ³¹P{¹H} NMR spectrum showed two singlets at δ = 20.3 (CPh₃) and –17.1 (OsPPh₃) ppm.

There are only two reported examples of azametallabenzene, that is, a tantalapyridine^[12a] and an osmapyridine.^[12b] Both reported metallapyridines are *o*-metallapyridines (**A**) in



which the nitrogen atom is directly bonded to the metal atom. In sharp contrast, the nitrogen atom in the metallacycle of **3** is bonded with carbon atoms (**B**, *m*-metallapyridine), which represents an unprecedented azametallabenzene system.

Remarkably, complex **3** reacts with copper(I) chloride to give complex **4** in 80% yield (Scheme 1). In this reaction, the S2 atom in **3** was abstracted and copper(I) chloride acted as a reductant, thus suggesting that the S2 atom does not have very strong bonding interactions with either C8 or the metal center. Complex **4** has been characterized by NMR spectroscopy and elemental analysis, as well as X-ray diffraction. In the ¹H NMR spectrum, the signal for the metallacycle unit OsCH was observed at δ = 12.0 ppm, and that of OsCHC(PPh₃)CH was obscured by the phenyl signals and thus assigned by ¹H–¹³C HSQC spectroscopy. The ¹³C{¹H} NMR spectrum displayed the signals of the three metal-bonded carbon atoms at δ = 258.1 (C8), 250.3 (C5), and 210.5 (C1) ppm. With the aid of ¹H–¹³C HSQC and C¹³-DEPT135 techniques, the ¹³C chemical shifts of the remaining carbon atoms of the metallacycles were located at δ = 136.6 (C7), 136.5 (C4), 125.8 (C3), and 109.6 (C2) ppm.

The molecular structure of **4** contains an essentially planar metal-bridged polycyclic structure (Figure 2). The mean deviation from the least-squares plane through Os1, N1, and C1–C8 is 0.0099 Å, and the maximum deviation from the least-squares plane through Os1, N1, and C1–C8 is 0.0202 Å for Os1. The Os–C8 bond length (1.894(4) Å) is appreciably longer than the typical Os≡C bond lengths (1.671–1.815 Å).^[13] The Os–C1 bond length (2.085(4) Å) is on the high end of the reported range for typical Os–C(vinyl) bond lengths (1.897–2.115 Å),^[13] and the Os–C5 bond length (1.954(4) Å) is within the range of typical Os=CH(carbene) bonds (1.732–2.050 Å).^[13] The bond distances of the C–C bonds in the metallacycle rings of **4** (1.338(5)–1.456(5) Å) are within the range of typical aromatic C–C bond lengths. The evident long/short C–C bond alternations are parallel to those found in other metallabenzynes, such as osmabenzene Os(≡CC–(SiMe₃)=C(CH₃)-C(NO₂)=CH)(PPh₃)₂Cl₂ [1.366(4)–

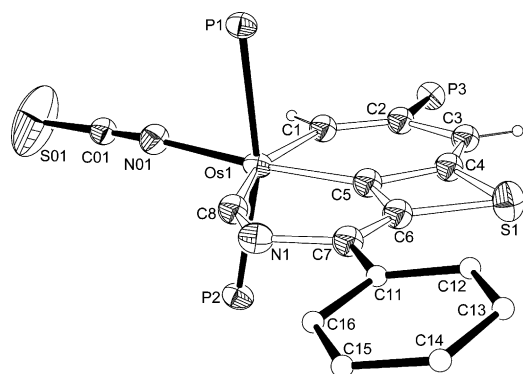
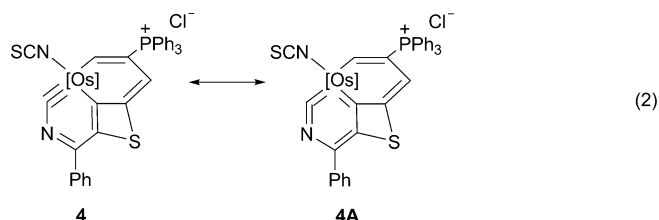
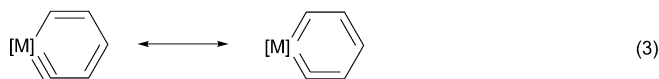


Figure 2. X-ray structure of complex **4**. Ellipsoids shown at the 50% probability level. Phenyl rings in PPh_3 groups, some of the hydrogen atoms and the counter anion are omitted for clarity. Selected bond distances [Å] and angles [°]: Os–C1 2.085(4), Os–C5 1.954(4), Os1–C8 1.894(4), C1–C2 1.360(5), C2–C3 1.456(5), C3–C4 1.338(5), C4–C5 1.456(5), C4–S1 1.794(4), C6–S1 1.785(4), C5–C6 1.447(5), C6–C7 1.355(5), C7–N1 1.416(5), C8–N1 1.236(5); C5–Os1–C1 83.65(14), C8–Os1–C5 75.89(15), Os1–C1–C2 132.9(3), C1–C2–C3 124.4(3), C2–C3–C4 118.6(3), C3–C4–C5 128.7(3), C4–C5–Os1 131.7(3), C6–S1–C4 74.22(17), C6–C5–C4 96.1(3), C5–C4–S1 94.5(2), C5–C6–S1 95.2(3), C6–C5–Os1 132.2(3), C7–C6–C5 127.1(4), C6–C7–N1 114.7(3), C8–N1–C7 118.7(3), N1–C8–Os1 151.4(3).

1.440(4) Å],^[6a] osmabenzynes $\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{CH}_3)-\text{C}(\text{NO})=\text{CH})(\text{PPh}_3)_2\text{Cl}_2$ [1.363(5)–1.451(5) Å],^[6a] and rhenabenzynes $\text{Re}(\equiv\text{CCH}=\text{C}(\text{tBu})\text{CH}=\text{CH})-(\text{PMe}_2\text{Ph})_3\text{Cl}$ [1.367(6)–1.457(6) Å].^[6b] The structural parameters indicate that the metallacycles of **4** could be represented by two resonance structures, namely **4** and **4A**, with **4A** being more important [Eq. (2)]. That outcome is not surprising as for



many other metallabenzynes similar resonance structures were commonly proposed to account for their structures [Eq. (3)].^[6] Complex **4** is also a polycyclic metallabenzonoid



aromatic compound and can be regarded as a metallaisoquinoline derivative.

It is worth mentioning that complexes **3** and **4** are air-stable. After being kept for months at room temperature, they remain nearly unchanged both in the solid state and in solution. Complexes **3** and **4** also have notable thermal stability. Solid samples of **3** or **4** can be heated at 100 °C in air for at least five hours without noticeable change. In our exploratory experiments, the reactivity of complex **4** was tested against a number of nucleophiles. Common nucleo-

philes such as H_2O , MeOH , MeONa , KOH , and NaSH do not react with **4**. In addition, complex **4** is also unreactive towards electrophiles such as HCl , HBF_4 , O_2 , MeI , and MeOTf .

We also carried out DFT calculations to evaluate the aromaticity related to the metallapyridine ring of complex **4**. The optimized structure of the model complex **4'**, in which PPh_3 groups were replaced by PH_3 , reproduces the structural features of **4** described above. The nucleus-independent chemical shift (NICS) values were computed for the metallapyridine ring. The calculated NICS values are $\delta = -4.5$ (NICS(0)) and -4.2 (NICS(1)) ppm. These values are comparable to those reported for other metallaaromatics.^[14] The aromatic stabilization energy (ASE) was also evaluated by employing the isomerization method introduced by Schleyer and Pühlhofer.^[15] Based on the model complex **4'**, in which the phenyl group on the metallapyridine ring was further replaced by a methyl group, an ASE of 11.3 kcal mol⁻¹ was calculated. The calculated ASE is at the lower end of the values obtained for other metallaaromatics.^[14b,16,17] The negative NICS values and the ASE calculated indicate aromaticity associated with the metallapyridine ring in complex **4**. More detailed results of the DFT calculations are given in the Supporting Information.

In summary, we have successfully synthesized the first *m*-metallapyridine and the first metallapyridine under mild reaction conditions. The two novel complexes reported here are metal-bridged polycyclic metallabenzonoid aromatics, in which the transition-metal center is shared by both six-membered rings. The synthetic method permits the use of metallabenzene as starting materials to access higher π -electron metallaaromatics. The preparation of other unique fused metallaaromatics is now ongoing.

Experimental Section

3: A mixture of **2** (500 mg, 0.39 mmol) and iodine (393 mg, 1.55 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for about 12 h to give a green solution. The volume of the mixture was reduced to about 2 mL under vacuum and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give complex **3** as a green solid. Yield: 421 mg, 65%. ^1H NMR (500.2 MHz, CDCl_3 , plus ^1H - ^{13}C HSQC): $\delta = 12.5$ (d, $J(\text{P,H}) = 22.3$ Hz, 1H, C^1H), 7.3 (d, $J(\text{P,H}) = 8.6$ Hz, 1H, C^3H), 6.8–7.9 ppm (m, 50H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): $\delta = 20.3$ (s, CPhPPh_3), -17.1 ppm (s, OsPPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3 , plus ^1H - ^{13}C HSQC and ^{13}C -dept 135): $\delta = 202.5$ (br, C^1), 222.2 (br, C^5), 198.6 (br, C^6), 146.8 (s, C^7), 144.0 (s, C^{10}), 127.6 (d, $J(\text{P,C}) = 18.9$ Hz, C^3), 135.0–118.4 (m, Ph), 136.1 (d, $J(\text{P,C}) = 13.0$ Hz, C^4), 108.8 (d, $J(\text{P,C}) = 83.2$ Hz, C^2), 124.2 ppm (s, C^6). C,H,N analysis calcd (%) for $\text{C}_{69}\text{H}_{52}\text{N}_2\text{S}_3\text{P}_3\text{I}_3\text{Os}$: C, 49.65; H, 3.14; N, 1.68. Found: C, 49.20; H, 3.17; N, 1.49.

4: A mixture of **3** (150 mg, 0.09 mmol) and copper(I) chloride (62 mg, 0.63 mmol) in CH_2Cl_2 (10 mL) was heated at reflux for about 2 d to give a dark green suspension. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (3 \times 5 mL). The volume of the filtrate was reduced to about 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (20 mL) to the residue produced a green solid, which was collected by filtration, washed with diethyl ether (3 \times 2 mL), and dried under vacuum. Yield: 93 mg, 80%. ^1H NMR (500.2 MHz, CD_2Cl_2): $\delta = 12.0$ (d, $J(\text{P,H}) = 30.1$ Hz, 1H, C^1H), 7.0–8.0 (m, 50H, Ph and C^3H (obscured by the phenyl signals and confirmed by ^1H - ^{13}C HSQC)). $^{31}\text{P}\{^1\text{H}\}$ NMR

(202.5 MHz, CD_2Cl_2): $\delta = 20.8$ (s, CPhPh_3), 7.5 ppm (s, OsPPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2 , plus HSQC and C^{13} -dept 135): $\delta = 210.5$ (br, C^1), 250.3 (br, C^5), 258.1 (br, C^8), 136.6 (s, C^7), 147.5 (s, C^{10}), 125.8 (d, $J(\text{P,C}) = 23.1$ Hz, C^3), 135.5–119.3 (m, Ph and C^6), 136.5 (d, $J(\text{P,C}) = 18.3$ Hz, C^4), 109.6 (d, $J(\text{P,C}) = 78.0$ Hz, C^2). $\text{C}_6\text{H}_5\text{N}_2\text{O}_2\text{S}_2\text{P}_3\text{ClO}_5$: C, 62.41; H, 4.25; N, 2.11. Found: C, 62.07; H, 4.49; N, 2.09.

Details of the preparation and characterization of **2** can be found in the Supporting Information.

Received: May 25, 2012

Published online: August 31, 2012

Keywords: aromaticity · metallacycles · osmium · structure elucidation · synthetic methods

- [1] a) R. Sanz, *Org. Prep. Proced. Int.* **2008**, 40, 215; b) D. Peña, D. Pérez, E. Guitián, *Heterocycles* **2007**, 74, 89; c) A. M. Dyke, A. J. Hester, G. C. Lloyd-Jones, *Synthesis* **2006**, 4093; d) H. Pellissier, M. Santelli, *Tetrahedron* **2003**, 59, 701; e) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.* **2003**, 115, 518; *Angew. Chem. Int. Ed.* **2003**, 42, 502.
- [2] a) S. S. Bhojgude, A. T. Biju, *Angew. Chem.* **2012**, 124, 1550; *Angew. Chem. Int. Ed.* **2012**, 51, 1520; b) D. Peña, D. Pérez, E. Guitián, *Angew. Chem.* **2006**, 118, 3659; *Angew. Chem. Int. Ed.* **2006**, 45, 3579; c) W. Sander, *Acc. Chem. Res.* **1999**, 32, 669, and references therein.
- [3] a) A. E. Goetz, S. M. Bronner, J. D. Cisneros, J. M. Melamed, R. S. Paton, K. N. Houk, N. K. Garg, *Angew. Chem.* **2012**, 124, 2812; *Angew. Chem. Int. Ed.* **2012**, 51, 2758; b) N. J. Rau, P. G. Wenthold, *J. Phys. Chem. A* **2011**, 115, 10353; c) M. Winkler, B. Cakir, W. Sander, *J. Am. Chem. Soc.* **2004**, 126, 6135; d) H.-H. Nam, G. E. Leroi, *J. Am. Chem. Soc.* **1988**, 110, 4096; e) K. M. Reinecke, *Tetrahedron* **1982**, 38, 427; f) T. Kauffmann, R. Wirthwein, *Angew. Chem.* **1971**, 83, 21; *Angew. Chem. Int. Ed. Engl.* **1971**, 10, 20, and references therein.
- [4] For recent reviews, see: a) M. Paneque, M. L. Poveda, N. Rendón, *Eur. J. Inorg. Chem.* **2011**, 19; b) G. Jia, *Coord. Chem. Rev.* **2007**, 251, 2167; c) J. R. Bleake, *Acc. Chem. Res.* **2007**, 40, 1035; d) L. J. Wright, *Dalton Trans.* **2006**, 1821; e) C. W. Landorf, M. M. Haley, *Angew. Chem.* **2006**, 118, 4018; *Angew. Chem. Int. Ed.* **2006**, 45, 3914; f) G. Jia, *Acc. Chem. Res.* **2004**, 37, 479; g) J. R. Bleake, *Chem. Rev.* **2001**, 101, 1205.
- [5] Recent examples for metallaaromatics: a) Q. Zhao, L. Gong, C. Xu, J. Zhu, X. He, H. Xia, *Angew. Chem.* **2011**, 123, 1390; *Angew. Chem. Int. Ed.* **2011**, 50, 1354; b) R. Lin, H. Zhang, S. Li, J. Wang, H. Xia, *Chem. Eur. J.* **2011**, 17, 4223; c) G. R. Clark, P. M. Johns, W. R. Roper, T. Söehnel, L. J. Wright, *Organometallics* **2011**, 30, 129; d) M. Baya, M. A. Esteruelas, E. Oñate, *Organometallics* **2011**, 30, 4404; e) H. Zhang, R. Lin, G. Hong, T. Wang, T. B. Wen, H. Xia, *Chem. Eur. J.* **2010**, 16, 6999; f) 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; g) P. M. Johns, W. R. Roper, S. D. Woodgate, L. J. Wright, *Organometallics* **2010**, 29, 5358; h) J. Huang, R. Lin, L. Wu, Q. Zhao, C. Zhu, T. B. Wen, H. Xia, *Organometallics* **2010**, 29, 2916; i) M. A. Esteruelas, I. Fernández, A. Herrera, M. Martín-Ortiz, R. Martínez-Álvarez, M. Oliván, E. Oñate, M. A. Sierra, M. Valencia, *Organometallics* **2010**, 29, 976; j) G. R. Clark, L. A. Ferguson, A. E. McIntosh, T. Söehnel, L. J. Wright, *J. Am. Chem. Soc.* **2010**, 132, 13443.
- [6] Examples for metallabenzynes: a) 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; b) 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; c) J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2011**, 123, 7433; *Angew. Chem. Int. Ed.* **2011**, 50, 7295; d) 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; e) 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; f) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, 127, 2856; g) 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; h) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem.* **2001**, 113, 2005; *Angew. Chem. Int. Ed.* **2001**, 40, 1951.
- [7] CCDC 828702 (**2**), 828703 (**3**), and 856993 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [8] G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811.
- [9] C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *Angew. Chem.* **2000**, 112, 766; *Angew. Chem. Int. Ed.* **2000**, 39, 750.
- [10] I. Novak, L. J. Harrison, W. Li, B. Kovač, *J. Phys. Chem. A* **2007**, 111, 2619.
- [11] F. Vögtle, *Fascinating Molecules in Organic Chemistry*, Wiley, Chichester, **1992**.
- [12] a) K. J. Weller, I. Filippov, P. M. Briggs, D. E. Wigley, *Organometallics* **1998**, 17, 322; b) 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.
- [13] Based on a search of the Cambridge Structural Database, CSD version 5.33 (November 2011).
- [14] a) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, 105, 3842; b) M. Mauksch, S. B. Tsogoeva, *Chem. Eur. J.* **2010**, 16, 7843; c) M. A. Iron, A. C. B. Lucassen, H. Cohen, M. E. van der Boom, J. M. L. Martin, *J. Am. Chem. Soc.* **2004**, 126, 11699; d) G. Periyasamy, N. A. Burton, I. H. Hillier, J. M. H. Thomas, *J. Phys. Chem. A* **2008**, 112, 5960.
- [15] P. von R. Schleyer, F. Pühlhofer, *Org. Lett.* **2002**, 4, 2873.
- [16] F. De Proft, P. Geerlings, *Phys. Chem. Chem. Phys.* **2004**, 6, 242.
- [17] I. Fernández, G. Frenking, *Chem. Eur. J.* **2007**, 13, 5873.