



Cite this: *Chem. Sci.*, 2018, 9, 5994

Received 10th May 2018
Accepted 18th June 2018

DOI: 10.1039/c8sc02086h

rsc.li/chemical-science

Facile synthesis of polycyclic metallaarynes†

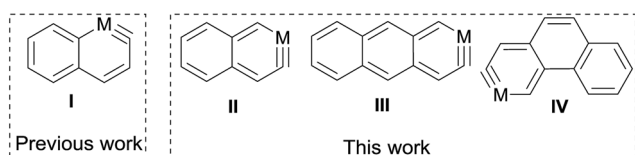
Wenqing Ruan,[‡] Tsz-Fai Leung,[‡] Chuan Shi, Ka Ho Lee, Herman H. Y. Sung, Ian D. Williams,^{ib*} Zhenyang Lin^{ib*} and Guochen Jia^{ib*}

Metalla-analogs of polycyclic arynes represent an interesting class of metallaaromatics with a formal M≡C bond within the ring. The first examples of a bicyclic β-metallaaryne and tricyclic metallaarynes, including a metallaanthracyne and a metallaphenanthryne, were obtained in good yields by reactions of OsCl₂(PPh₃)₃ with alkyne-functionalized phosphorus ylides.

Introduction

There has been much interest in the development of the chemistry of aromatic metallacycles of transition metals.¹ Monocyclic six-membered metallacycles such as metalbenzenes and metallabenzynes are among the most well-studied aromatic metallacycles.² More recently, aromatic metallacycles with a more extended structure have been attracting considerable attention.³

Polycyclic arenes and arynes are an important class of aromatic organic compounds with an extended conjugation system. Thus, it is naturally desirable to develop the chemistry of metalla-analogs of such compounds. These compounds are attractive considering the interesting material properties of polycyclic aromatic hydrocarbons and hetero-arenes containing a main group element.⁴ However, limited progress has been made in this direction. Well-characterized polycyclic metallaarenes are confined to a few bicyclic metallanaphthalenes (of iridium⁵ and osmium⁶) and a tricyclic iridaanthracene.⁷ Reported polycyclic metallaarynes are even more rare and are limited to two bicyclic α-osmanaphthalynes^{6,8} (derivatives of α-metallanaphthalene I, Scheme 1).



Scheme 1 Structures of selected examples of polycyclic metallaarynes.

Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. E-mail: chwill@ust.hk; chzlin@ust.hk; chjiag@ust.hk

† Electronic supplementary information (ESI) available. CCDC 1589937, 1589938, and 1831065. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc02086h

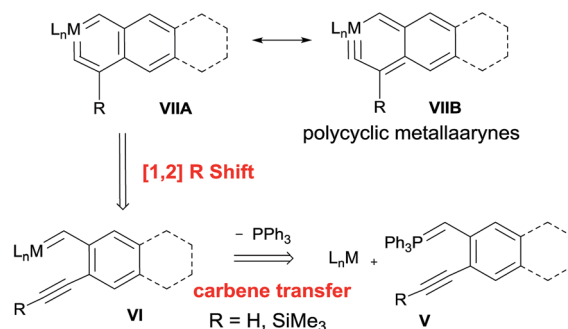
‡ These authors contributed equally to this work.

In this work, we report a versatile synthetic method for the synthesis of polycyclic metallaarynes, which enabled us to prepare the first examples of a bicyclic β-metallanaphthalene (II) and tricyclic metallaarynes including a metallaanthracene (III) and a metallaphenanthryne (IV) (Scheme 1).

The development of the chemistry of polycyclic metallaarynes has been hindered by the lack of efficient routes to synthesize such compounds. Although two α-osmanaphthalynes have been prepared by cyclometallation of a phenyl ring in the vinylcarbyne complexes (PPh₃)₂Cl₃Os{≡CCH=C(*o*-C₆H₄Cl)₂} (induced by Zn)⁸ and (PPh₃)₂Cl₂HOs{≡CC(PPh₃)=CHPh}BF₄ (induced by oxygen),^{6a} this cyclometallation strategy could not be easily extended to prepare polycyclic metallaarynes with a metal in the β-position or with a more extended structure due to the lack of generality of the cyclometallation reactions, or the difficulty in obtaining the necessary precursor complexes. We have therefore searched for alternative and more general routes to prepare polycyclic metallaarynes, and explored the possibility of synthesizing polycyclic metallaarynes from alkyne-functionalized phosphorus ylides.

Results and discussion

The strategy was devised on the basis of the retrosynthetic analysis shown in Scheme 2. It is known that phosphorus ylides



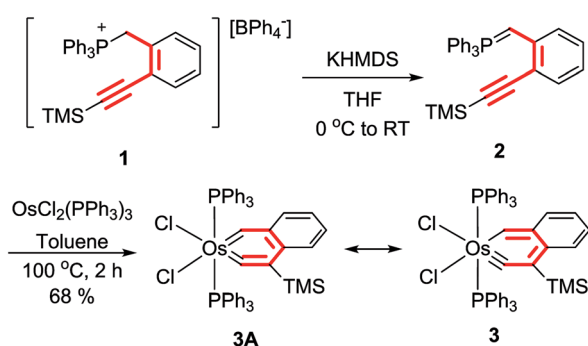
Scheme 2 Retrosynthesis of polycyclic metallaarynes.



can act as genuine carbene transfer agents⁹ and that alkyne complexes $L_nM(R'C\equiv CR)$ ($R = H$,¹⁰ $SiMe_3$ (ref. 11)) can rearrange to give vinylidene complexes $L_nM\{=C=C(R')(R)\}$ *via* a 1,2-R shift. We therefore envisioned that polycyclic metallaryne complex **7** might be obtained from rearrangement of carbene intermediate **VI** which was generated from the reaction of alkyne-functionalized phosphorus ylide **V** with a coordinatively unsaturated complex L_nM .

To verify the hypothesis, we have studied the reactions of $OsCl_2(PPh_3)_3$ with the ylides $o-C_6H_4(C\equiv CR)(CH=PPh_3)$ ($R = H$, $SiMe_3$), which can be obtained from the phosphonium salt $[o-C_6H_4(C\equiv CSiMe_3)(CH_2PPh_3)]BPh_4$ (**1**) (Scheme 3). The ylide $o-C_6H_4(C\equiv CH)(CH=PPh_3)$ was obtained by treatment of **1** with two equiv. of $PhCH_2K$ followed by one equiv. of 2,6-lutidinium tetraphenylborate, and the ylide $o-C_6H_4(C\equiv CSiMe_3)(CH=PPh_3)$ (**2**) was obtained by the reaction of **1** with one equiv. of potassium hexamethyldisilazide (KHMDS). The ylide $o-C_6H_4(C\equiv CH)(CH=PPh_3)$ reacted with $OsCl_2(PPh_3)_3$ in toluene at room temperature or 110 °C to give a mixture of highly sensitive and intractable species. To our delight, the treatment of $OsCl_2(PPh_3)_3$ with the ylide $o-C_6H_4(C\equiv CTMS)(CH=PPh_3)$ (**2**) in toluene at 110 °C for 2 h gave the expected osmanaphthalene **3**, which was isolated as a green solid in 68% yield (Scheme 3). Apparently, the $SiMe_3$ -containing osmanaphthalene **3** has higher stability or lower reactivity than the analogous desilylated osmanaphthalene. Indeed, early computational studies have revealed that a silyl group on the carbon adjacent to the carbyne carbon can increase the conjugation energy of metallabenzynes¹² and increase the stability of the metallabenzynes with respect to the formation of the corresponding carbene complexes.¹³ In addition, the silyl group could also decrease the reactivity of the carbyne carbon with nucleophiles.

The structure of complex **3** was confirmed by X-ray diffraction analysis (Fig. 1),¹⁴ which reveals that complex **3** has an essentially planar metallacycle. The angle around the carbyne carbon ($153.1(5)^\circ$) is similar to those found in reported metallabenzynes.¹⁵ The Os–C1 (carbyne) bond distance ($1.826(6)$ Å) of **3** is appreciably longer than those of typical $Os\equiv C$ bonds (1.69 – 1.79 Å) and at the low end of those observed for $L_nOs=C=CRR'$ complexes (1.786 – 1.892 Å), while the Os–C5 bond distance ($1.963(6)$ Å) is within the range of Os–C (vinyl) bonds (1.897 – 2.195 Å).¹⁵ The structural data indicate that the vinylidene resonance form **3A** makes a significant contribution to the overall structure of the osmanaphthalene.



Scheme 3 Synthesis of the β -metallaphthalene complex **3**.

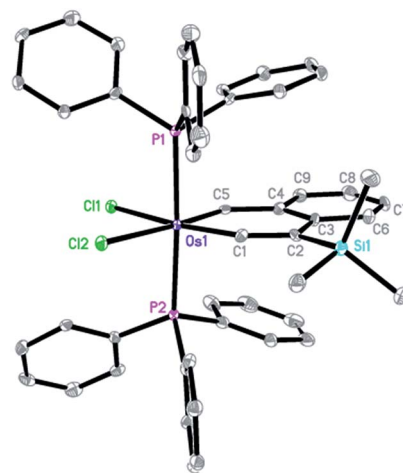
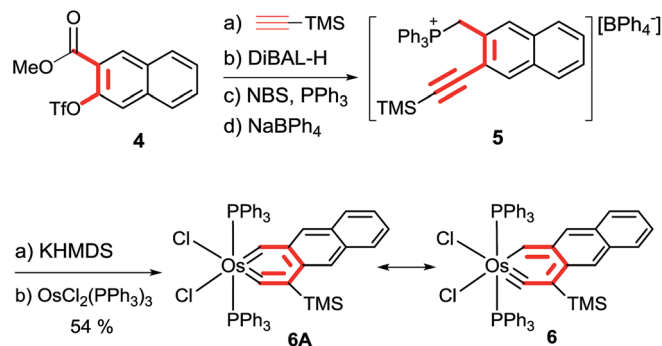


Fig. 1 X-ray crystal structure of **3** (ellipsoids at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1–C1, $1.826(6)$; Os1–C5, $1.963(6)$; C1–Os1–C5, $79.5(2)$; Os1–C1–C2, $153.1(5)$.

The solid state-structure of complex **3** is supported by the solution NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at -2.9 ppm for the two equivalent PPh_3 ligands. The $^{13}C\{^1H\}$ NMR spectrum displayed signals of OsC1 ($Os\equiv C$) and OsC5 ($OsCH$) at 308.0 and 277.6 ppm, respectively. In the 1H NMR spectrum, the $OsCH$ signal was observed at 15.76 ppm.

Having succeeded in isolating the β -osmanaphthalene **3**, we tried to extend the chemistry to larger polycyclic metallarynes, starting with tricyclic systems. There are two types of tricyclic metallarynes: (i) metallanthracenes and (ii) metallaphenanthrynes, which are derived respectively from anthracene and phenanthrene, the simplest 'linear' and 'bent' triarenes.

Preparation of a metallanthracene was first pursued. The required phosphonium salt **5** was obtained by the Sonogashira coupling reaction of ester **4** with $HC\equiv CTMS$ to give an alkyne derivative, followed by sequential treatment of the derivative with DiBAL-H, NBS/ PPh_3 and $NaBPh_4$ (Scheme 4). Treatment of **5** with KHMDS generated an ylide which reacted smoothly with $OsCl_2(PPh_3)_3$ in toluene at 110 °C to give the desired osmananthracene **6**, which was isolated as a yellow solid in 54% yield.



Scheme 4 Synthesis of the metallanthracene complex **6**.

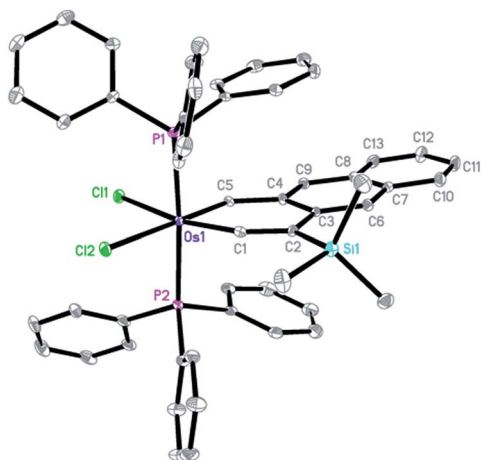


Fig. 2 X-ray crystal structure of **6** (ellipsoids at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1–C1, 1.816(6); Os1–C5, 1.964(6); C1–Os1–C5, 79.2(2); Os1–C1–C2, 153.7(5).

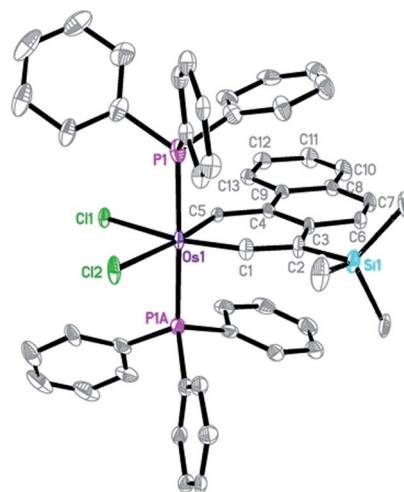


Fig. 3 X-ray crystal structure of **9** (ellipsoids at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1–C1, 1.791(7); Os1–C5, 2.002(6); C1–Os1–C5, 78.7(3); Os1–C1–C2, 153.7(6).

Complex **6** was characterized by NMR and elemental analysis. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a singlet at -7.0 ppm for the two equivalent PPh_3 ligands. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displayed the signals of $\text{Os}\equiv\text{C}$ and OsCH at 304.1 and 288.4 ppm, respectively. In the ^1H NMR spectrum, the OsCH signal was observed at 16.51 ppm. The chemical shifts of the ^1H and ^{13}C signals of **6** are similar to those of **3**.

The structure of complex **6** was also confirmed by X-ray diffraction analysis (Fig. 2). Complex **6** can be viewed as a compound formed by annulation of a benzene ring to the metallanaphthalene structural unit of **3**. The X-ray data indicate that the annulation does not alter the structural parameters of the metallanaphthalene structural unit significantly. For example, the Os–C bond distances as well as the bond angle around the carbyne carbon of **6** are similar to those observed for **3**.

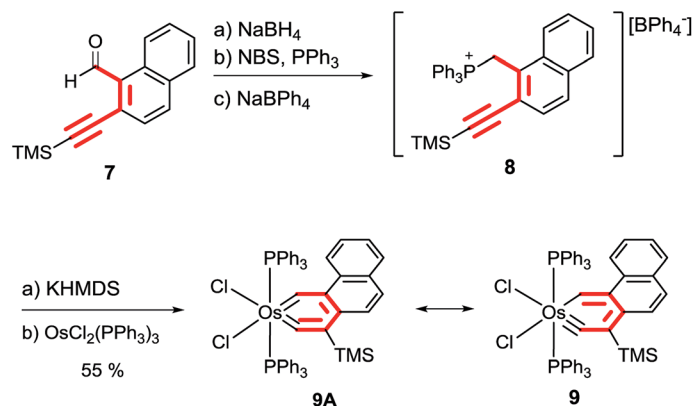
The methodology could also be extended to synthesize metallaphenanthrynes. As shown in Scheme 5, treatment of the aldehyde derivative **7** with NaBH_4 followed by NBS/ PPh_3 and NaBPh_4 produced the phosphonium salt **8**. The ylide generated from the reaction of phosphonium salt **8** with KHMDs reacted

smoothly with $\text{OsCl}_2(\text{PPh}_3)_3$ in toluene at 110°C to give the osmaphenanthryne **9** which was isolated as a green solid in 55% yield.

The identity of complex **9** has been confirmed by the NMR and analytical data as well as X-ray diffraction analysis (Fig. 3). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **9** showed a singlet at -0.37 ppm. Characteristic ^{13}C signals of $\text{Os}\equiv\text{C}$ and OsCH were observed respectively at 308.1 and 250.9 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. In the ^1H NMR spectra, the OsCH signal was observed at 16.14 ppm.

The X-ray diffraction analysis of complex **9** confirms that it has a planar metallacycle. Subtle differences were noted in the structural parameters of the osmanthracene **6** and the osmaphenanthryne **9**, which are structural isomers. The Os–C1 (carbyne) bond distance (1.791(7) Å) of **9** is appreciably shorter than that (1.826(6) Å) of **6** while the Os–C5 bond distance (2.002(6) Å) of **9** is appreciably longer than that (1.963(6) Å) of **6**.

The structural data indicate that, compared with the case of **6**, the vinylidene resonance form **9A** makes a lower contribution to the overall structure of the osmaphenanthryne **9**.



Scheme 5 Preparation of the osmaphenanthryne **9**.

Complexes **6** and **9** are interesting as they represent the first examples of tricyclic metallaarynes. In fact, even well-characterized tricyclic metallaarenes are rare. Wright and his co-workers recently reported the isolation and structural characterization of the first metallaanthracene, an iridaanthracene.⁷ Jones and his co-workers generated a thermally unstable lithiated ruthenaphenanthrene oxide that could only be characterized spectroscopically at low temperature and reacted with Et_3OBF_4 to give an η^3 -benzyl complex.¹⁶ In related work, Bettinger and his co-workers found that thermolysis of 9-azido-9-borabluorene produced a reactive 9,10-BN-phenanthryne which undergoes a self-trapping reaction to give a cyclic tetramer.¹⁷

Our complexes **3**, **6** and **9** are metalla-analogs of β -naphthalene, anthracene and phenanthryne, respectively. Similarities in the structural properties of the metallacycles and their organic counterparts are noted. In particular, they have the same bond alternation pattern and similar corresponding C–C bond distances when the C–Os–C fragment in the metallacycles and the C–C \equiv C fragment in the organic counterparts are excluded (see Fig. S28–30 in the ESI†). Naphthalene, anthracene and phenanthryne are aromatic. Our DFT calculations confirm that all the rings of complexes **3**, **6** and **9** have negative NICS(1) values¹⁸ (see Fig. S31 in the ESI†), indicating that the aromatic character is retained when a carbon atom in a polycyclic aryne is replaced by an isolobal metal fragment.

It is interesting to note that polycyclic aryne and their metalla-analogs show different thermal stabilities. Naphthalynes,¹⁹ anthracynes²⁰ and phenanthrynes²¹ are too reactive to be isolated in the free-state and have only been detected in argon matrices at low temperature. In contrast, complexes **3**, **6** and **9** are air-stable species which can be stored in the solid form for months without appreciable decomposition. The higher stability of **3**, **6** and **9** could be related to the fact that the ring strains of **3**, **6** and **9** are smaller than those of their organic counterparts as significant bond bending occurs at only one carbon in **3**, **6** and **9** (from 180° to ca. 153°), but at two carbons

in the organic compounds with an even larger bending angle (from 180° to ca. 127°).

Preliminary reactivity studies reveal that polycyclic metallaarynes can also possess chemical properties different from those of polycyclic arenes and metallaarenes. For example, anthracene²² and iridaanthracene **12** (ref. 7) have been reported to undergo $[4 + 2]$ cycloaddition reactions with maleic anhydride at the central ring (in refluxing benzene or 1,2-dichloroethane, respectively) (Scheme 6). In contrast, essentially no reaction was observed when a mixture of the osmaanthracene **6** and maleic anhydride (in a 1 : 4 molar ratio) was heated in benzene at 80°C for 3.5 h, suggesting that the central ring of the osmaanthracene is less reactive than those of anthracene and the iridaanthracene.

Conclusions

In summary, we have developed a convenient synthetic route to polycyclic metallaarynes. Through reactions of $\text{OsCl}_2(\text{PPh}_3)_3$ with alkyne-functionalized phosphorus ylides, we have successfully prepared the first examples of β -metallanaphthalene, metallaanthracene and metallaphenanthryne complexes. Reactivity studies of the new metallacycles as well as the preparation of polycyclic metallaarynes with other metals or with a more extended structure utilizing the phosphorus-ylide strategy are now underway.

Conflicts of interest

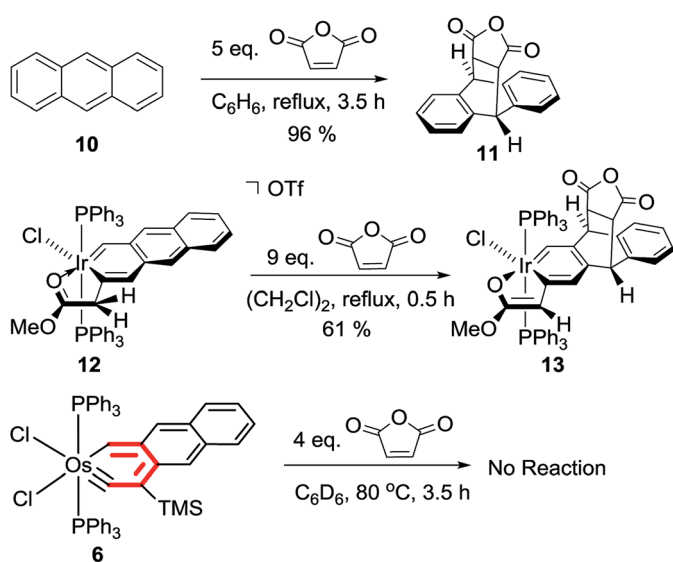
There are no conflicts to declare.

Acknowledgements

This work was supported by the Hong Kong Research Grants Council (Project No. 602113 and 16321516).

Notes and references

- (a) B. J. Frogley and L. J. Wright, *Chem.-Eur. J.*, 2018, **24**, 2025–2038; (b) J. Wei, W. X. Zhang and Z. Xi, *Chem. Sci.*, 2018, **9**, 560–568.
- For a recent review, see: L. J. Wright, *Metallabenzenes: An Expert View*, John Wiley & Sons Ltd, Oxford, 2017.
- For examples of recent work, see: (a) C. Zhu, J. Zhu, X. Zhou, Q. Zhu, Y. Yang, T. B. Wen and H. Xia, *Angew. Chem., Int. Ed.*, 2018, **57**, 3154–3157; (b) R. Li, Z. Lu, Y. Cai, F. Jiang, C. Tang, Z. Chen, J. Zheng, J. Pi, R. Zhang, J. Liu, Z. Chen, Y. Yang, J. Shi, W. Hong and H. Xia, *J. Am. Chem. Soc.*, 2017, **139**, 14344–14347; (c) M. Luo, L. Long, H. Zhang, Y. Yang, Y. Hua, G. Liu, Z. Lin and H. Xia, *J. Am. Chem. Soc.*, 2017, **139**, 1822–1825; (d) C. Zhu, J. Wu, S. Li, Y. Yang, J. Zhu, X. Lu and H. Xia, *Angew. Chem., Int. Ed.*, 2017, **56**, 9067–9071; (e) Y. Zhang, J. Wei, Y. Chi, X. Zhang, W. X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2017, **139**, 5039–5042; (f) J. Wei, Y. Zhang, Y. Chi, L. Liu, W. X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2016, **138**, 60–63; (g) M. Batuecas, R. Castro-Rodrigo, M. A. Esteruelas, C. Garcia-Yebra,



Scheme 6 Reactions with maleic anhydride.



- A. M. Lopez and E. Onate, *Angew. Chem., Int. Ed.*, 2016, **55**, 13749–13753.
- 4 (a) M. Stepien, E. Gonka, M. Zyla and N. Sprutta, *Chem. Rev.*, 2017, **117**, 3479–3716; (b) *Polycyclic Arenes and Heteroarenes: Synthesis Properties, and Applications*, ed. Q. Miao, Wiley-VCH, Weinheim, 2016.
- 5 (a) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate and K. Mereiter, *J. Am. Chem. Soc.*, 2003, **125**, 9898–9899; (b) M. Talavera, S. Bolaño, J. Bravo, J. Castro, S. García-Fontán and J. M. Hermida-Ramón, *Organometallics*, 2013, **32**, 4058–4060; (c) A. Vivancos, Y. A. Hernández, M. Paneque, M. L. Poveda, V. Salazar and E. Álvarez, *Organometallics*, 2015, **34**, 177–188.
- 6 (a) B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. B. Wen, Z. Cao and H. Xia, *Angew. Chem., Int. Ed.*, 2009, **48**, 5461–5464; (b) For theoretical studies, see: J. I. Fan, X. R. Wang and J. Zhu, *Organometallics*, 2014, **33**, 2336–2340.
- 7 B. J. Frogley and L. J. Wright, *Angew. Chem., Int. Ed.*, 2017, **56**, 143–147.
- 8 G. He, J. Zhu, W. Y. Hung, T. B. Wen, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Angew. Chem., Int. Ed.*, 2007, **46**, 9065–9068.
- 9 See for example: (a) J. Vignolle, B. Donnadiou, D. Bourissou, M. Soleilhavoup and G. Bertrand, *J. Am. Chem. Soc.*, 2006, **128**, 14810–14811; (b) L. R. Falvello, R. Llusar, M. E. Margalejo, R. Navarro and E. P. Urriolabeitia, *Organometallics*, 2003, **22**, 1132–1144; (c) L. K. Johnson, M. Frey, T. A. Ulibarri, S. C. Virgil, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 8167–8177.
- 10 (a) J. A. Varela, C. González-Rodríguez and C. Saá, *Top. Organomet. Chem.*, ed. C. Bruneau and P. Dixneuf, Springer, Cham, 2014, vol. 48, pp. 237–287; (b) J. M. Lynam, *Chem.-Eur. J.*, 2010, **16**, 8238–8247.
- 11 See for example: (a) K. Ilg, M. Paneque, M. L. Poveda, N. Rendón, L. L. Santos, E. Carmona and K. Mereiter, *Organometallics*, 2006, **25**, 2230–2236; (b) M. V. Jiménez, E. Sola, F. J. Lahoz and L. A. Oro, *Organometallics*, 2005, **24**, 2722–2729; (c) D. Huang, W. E. Streib, O. Eisenstein and K. G. Caulton, *Organometallics*, 2000, **19**, 1967–1972.
- 12 S. Ng, X. Huang, T. Wen, G. Jia and Z. Lin, *Organometallics*, 2003, **22**, 3898–3904.
- 13 J. Fan, K. An, X. Wang and J. Zhu, *Organometallics*, 2013, **32**, 6271–6276.
- 14 CCDC 1589937, 1589938, and 1831065 contain the supplementary crystallographic data for this paper.
- 15 G. Jia, *Coord. Chem. Rev.*, 2007, **251**, 2167–2187.
- 16 J. Yang, W. M. Jones, J. K. Dixon and N. T. Allison, *J. Am. Chem. Soc.*, 1995, **117**, 9776–9777.
- 17 M. Müller, C. Maichle-Mössmer and H. F. Bettinger, *Angew. Chem., Int. Ed.*, 2014, **53**, 9380–9383.
- 18 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.
- 19 (a) A. Comandini, S. Abid and N. Chaumeix, *J. Phys. Chem. A*, 2017, **121**, 5921–5931; (b) T. Sato, H. Niino and A. Yabe, *J. Phys. Chem. A*, 2001, **105**, 7790–7798; (c) J. Cioslowski, P. Piskorz and D. Moncrieff, *J. Am. Chem. Soc.*, 1998, **120**, 1695–1700; (d) T. Kitamura, N. Fukatsu and Y. Fujiwara, *J. Org. Chem.*, 1998, **63**, 8579–8581.
- 20 (a) A. Comandini, S. Abid and N. Chaumeix, *J. Phys. Chem. A*, 2017, **121**, 5921–5931; (b) J. Cioslowski, P. Piskorz and D. Moncrieff, *J. Am. Chem. Soc.*, 1998, **120**, 1695–1700; (c) R. Camenzind and B. Rickborn, *J. Org. Chem.*, 1986, **51**, 1914–1916.
- 21 H. Tomioka, A. Okuno, T. Sugiyama and S. Murata, *J. Org. Chem.*, 1995, **60**, 2344–2352.
- 22 W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, 1938, **60**, 481–485.

