ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2019, 55, 6237

Received 3rd April 2019,
Accepted 3rd May 2019

DOI: 10.1039/c9cc02594d

rsc.li/chemcomm

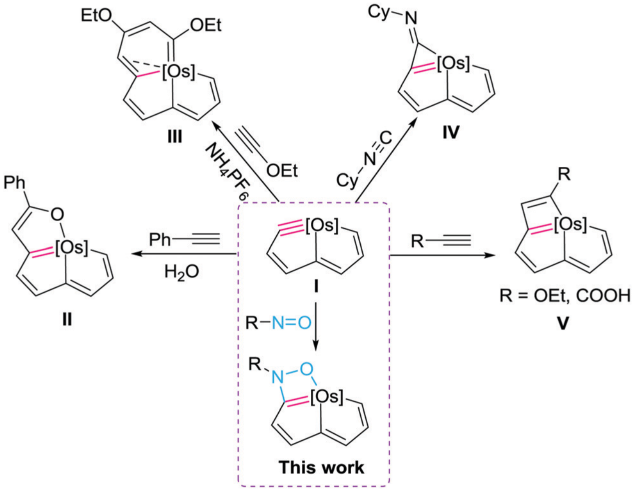
Synthesis and characterization of metallapentalenoxazetes by the [2+2] cycloaddition of metallapentalynes with nitrosoarenes†

Zhihong Deng,[a] Congqing Zhu,[b] Yuhui Hua,[b] Guomei He,[a] Ying Guo,[b] Ruqiang Lu,[b] Xiaoyu Cao,[b] Jiangxi Chen*[a] and Haiping Xia*[bc]

Cycloaddition reactions of carbynes in metallacycles with π-bond substrates have been rarely reported. We report the first [2+2] cycloaddition of metallapentalynes with nitrosoarenes to obtain the first metallapentalenoxazetes, and their photophysical and electrochemical properties were studied by UV-Vis spectroscopy and cyclic voltammetry with the help of theoretical calculations.

Conjugated metallacycles, such as metallabenzenes,[1,2] metallabenzynes,[3,4] and others,[5,6] display properties of both organometallics and organic carbocycles. For example, metallapentalyne **I** (Scheme 1),[7] a planar Craig-type Möbius metalla-aromatic,[8] exhibits rich metal carbyne reactivities due to the extreme strain in the fused five-membered ring containing a metal carbyne bond. This carbyne unit in **I** readily reacts with triple-bond substrates under various conditions to afford a series of "carbolong" complexes.[9] For instance, its reaction with phenylacetylene in the presence of water leads to the α-metallapentalenofuran **II**.[10] It can also undergo a [2+2+2] cycloaddition reaction with excess HC≡C–OEt to produce a tricyclic eleven-carbon framework **III**.[11] Interestingly, the osmacyclopropenimine **IV** was generated from the reaction of osmapentalyne **I** with isocyanide,[12] and the [2+2] cycloadditions of osmapentalyne with terminal alkynes in the absence of additives occurred smoothly to form cyclobutaosmapentalenes **V**.[13]

Conjugated metallacycles display very interesting properties. For example, it has been reported that "carbolong" complexes can exhibit good performance in near-infrared (NIR) absorption,[14] aggregation-enhanced photoluminescence,[7a] single molecular conductance,[15] and photothermal and photoacoustic effects.[13,16]



Scheme 1 Reactions of osmapentalyne with π-bond substrates.

These results motivated us to explore the reactivity of the osmapentalyne **I** towards organic substrates containing π-bonds, and to study the properties of the resulting products. Thus, when the osmapentalyne **1** was mixed in one-pot with olefins including styrene, cyclohexene, and 1-bromopropene or imines such as benzalmethylamine, no reaction was observed. When nitrosobenzene was used, however, the cycloaddition reaction occurred smoothly and cleanly.

Herein, we present the first [2+2] cycloaddition reaction of metallapentalynes with nitrosoarenes (Ar–N=O) to obtain air stable metallapentalenoxazetes, and their spectroscopic and electrochemical properties were also studied.

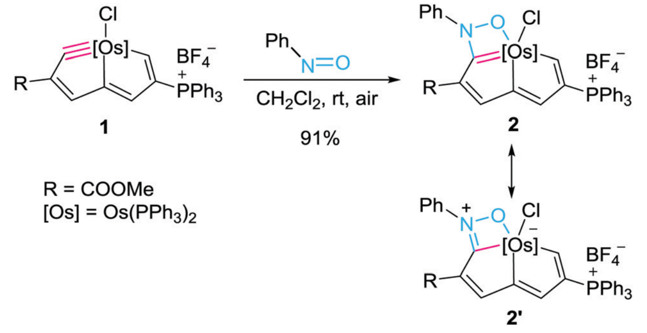
As shown in Scheme 2, treatment of osmapentalyne **1** with nitrosobenzene in dichloromethane at room temperature in air led to the formation of complex **2**, which was isolated as a red solid in 91% yield.

The structure of **2** has been determined by X-ray diffraction. As shown in Fig. 1, the metal center in **2** is shared by three metallacycles, the bicyclic metallapentalene unit and

---

[a] *Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, People's Republic of China. E-mail: chenjx@xmu.edu.cn*
[b] *College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China. E-mail: hpxia@xmu.edu.cn*
[c] *Department of Chemistry, Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen 518055, People's Republic of China*

† Electronic supplementary information (ESI) available. CCDC 1890223 and 1890305. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc02594d



Scheme 2 The [2+2] cycloaddition of osmapentalyne **1** with nitrosobenzene to afford complex **2**.

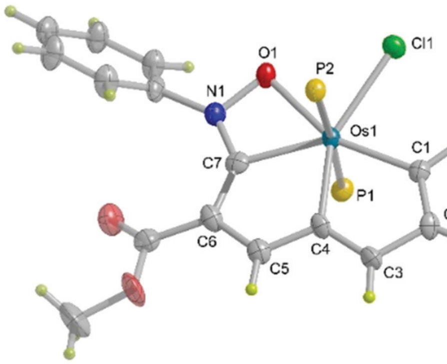


Fig. 1 X-ray crystal structure of the cation of **2** (thermal ellipsoids are set at the 50% probability level and the phenyl groups in the PPh_3 moieties are omitted for clarity). Selected bond lengths [Å] and angles [°]: Os1–C1: 2.070(10), Os1–C4: 2.127(9), Os1–C7: 2.078(10), Os1–O1: 2.146(7), N1–O1: 1.389(11), C7–N1: 1.296(13), C4–Os1–C1: 72.0(4), C7–Os1–C4: 71.4(4), C7–Os1–O1: 61.4(3), Os1–O1–N1: 92.9(5), and O1–N1–C7: 106.8(8).

the metallaoxazete unit. The geometry of **2** can be viewed as a pentagonal bipyramid in which the equatorial plane is occupied by three carbon atoms (C1, C4, and C7), one oxygen atom, and one chlorine atom. The bond distances of Os1–C1 (2.070 Å) and Os1–C7 (2.078 Å) are slightly shorter than that of Os1–C4 (2.127 Å) (Table S3, ESI†), but similar to those reported for metallapentalenes (1.907–2.175 Å).[17] The bond length of Os1–O1 (2.146 Å) is similar to that of the Os–O single bond in osmafurans.[18] The C–C bond lengths (1.345–1.454 Å) in the metallapentalene framework are in the usual range of single and double bonds. The N1–O1 and C7–N1 bond lengths are 1.389 and 1.296 Å, respectively.

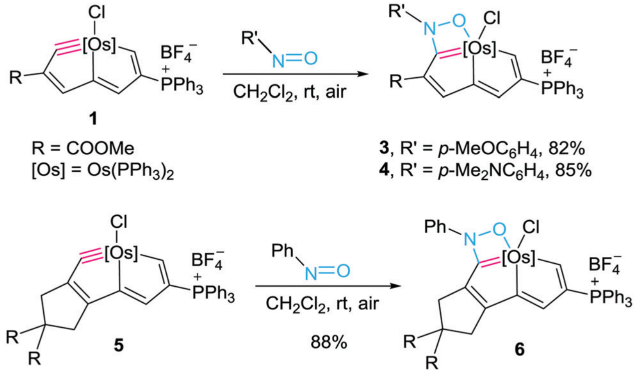
Complex **2** was further characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS). The ^1H NMR spectrum displays the Os–CH (H1) signal at 12.65 ppm as a doublet, and the signals from H3 and H5 are located in the aromatic region at 7.70 and 7.49 ppm, respectively. The ^{13}C NMR spectrum displays the signals of the three metal-bound carbons at 210.93 (C1), 178.04 (C4), and 173.30 (C7) ppm. The signals of the remaining carbons in the metallacycle are observed at 163.44 (C5), 146.24 (C3), 144.69 (C6), and 118.92 (C2) ppm. The ^{31}P NMR spectrum shows two singlets, at 10.84 ($CPPh_3$) and −14.87 ppm ($OsPPh_3$). The HRMS spectrum of **2** shows a prominent molecular ion at m/z = 1266.2755, which was attributed to **2** (calculated m/z = 1266.2767).

There are two major resonance forms of complex **2**: the neutral osmapentalenoxazete **2** and the zwitterionic form **2′**. The N–C and N–O bond distances, and the chemical shifts of the metal-bound carbons attached to the osmium indicate that zwitterion **2′** makes a significant contribution to the hybrid structure of **2**, in which two unstable organic frameworks, oxazete and pentalene,[19] are simultaneously stabilized by incorporation of a metal fragment (Scheme 2).

The reactants concerned in this [2+2] cycloaddition reaction can be extended as shown in Scheme 3. For example, when *p*-nitrosoanisole or *p*-nitroso-*N*,*N*-dimethyl-aniline was used, complexes **3** and **4** were isolated in a high yield. When osmapentalyne (**1**) was replaced by **5**, the reaction of **5** with nitrosobenzene also occurred smoothly and cleanly to afford complex **6** as an orange solid in 88% yield (Scheme 3). Complex **6** was also characterized by single crystal X-ray crystallography (Fig. S2, ESI†). The bond distances and angles of the three metallacycles in **6** are almost identical to those in **2** (Table S4, ESI†). The four cycles (the three metallacycles and the fused-cyclopentene ring) are coplanar, as reflected by their small mean deviation (0.025 Å) from the least squares plane. The NMR and HRMS spectral data of **6** are in agreement with its molecular structure.

Notably, the introduction of electron-donating substituents at the *para*-position of the nitrosophenyl ring significantly accelerates the reaction rate, and this can be attributed to the increasing nucleophilicity of the nitrogen atom. This result suggests that the reaction pathway probably involves an initial nucleophilic addition of the nitrogen atom to the carbyne carbon of the osmapentalyne, and this is followed by intramolecular ring closure to afford the metallapentalenoxazete.[20]

The [2+2] cycloaddition between the metal carbyne and the alkyne is an initial step in alkyne metathesis,[21] and has attracted significant attention. A few reactions between metal carbynes and alkenes or other double bond containing substrates have been reported.[20,22] For example, the "ynene" metathesis between tungsten carbynes and alkenes lead to polyolefins through the initial formation of metallacyclobutadiene.[22a,b] To the best of our knowledge, only one closely related cycloaddition between acyclic



Scheme 3 The cycloaddition of osmapentalynes with nitrosoarenes.

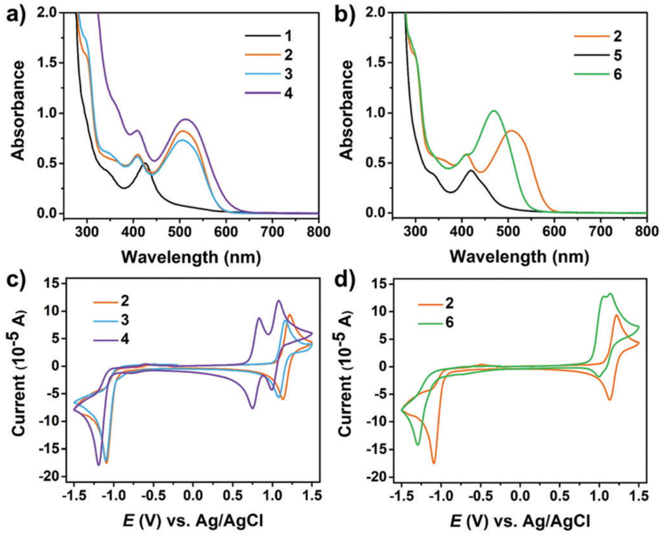


Fig. 2 UV-Vis spectra (CH_3CN, 1 × 10^{-4} M, room temperature) of (a) osmapentalyne **1** and its cycloaddition derivatives **2–4** and (b) **2**, **5** and **6**. Cyclic voltammograms of (c) cycloaddition derivatives **2–4** and (d) **2** and **6** in CH_3CN.

metal carbynes and a C-nitroso compound (*t*BuN═O) has been reported.[22c] Our reaction provides a new [2+2] cycloaddition involving a novel metal carbyne in the metalla-aromatic ring. In addition, the resulting complexes **2–4** and **6** are remarkably stable in air, moisture, and heat. When they are stored in air up to 160 °C for at least 15 h (Table S6, ESI†), no applicable changes are observed. This allows us to study their photophysical and redox properties.

As shown in Fig. 2a, the UV-Vis absorption spectra of **2–4** display absorption maxima at λ_{max} = 507, 509, and 513 nm, respectively, which are obviously red-shifted relative to the spectrum of osmapentalyne **1**. To understand the absorption spectra further, TD-DFT calculations were performed at the B3LYP/6-31+g(d) level (for details see the ESI†). The lowest unoccupied molecular orbitals (LUMOs) of compounds **2–4** are mainly localized in the three metallacycles, while the highest occupied molecular orbitals (HOMOs) are distributed in the whole molecule, with the exception of the PPh_3 moieties (Table S1, ESI†). In addition, incorporation of methoxyl or *N*,*N*-dimethyl groups, electron-donating substituents, into the phenyl ring can gradually raise the energy levels of both HOMO and LUMO, and narrow the energy gaps (ΔE). The computed results show that the excitations of **2–4** mainly occur from HOMOs to LUMOs (Table S2, ESI†), and agree with those shown in the UV-Vis spectra. Thus, the absorption curve of **2** is comparable to that of **3**, while **4** exhibits a slight red-shift of the absorption. In particular, complex **6**, bearing an additional fused cyclopentene unit, displays a broad ΔE as a result of the higher LUMO level. The absorption maximum of **6** at λ_{max} = 468 nm can be attributed to the transitions of HOMO → LUMO (63%) and HOMO−4 → LUMO (24%) (Table S2, ESI†), and is blue-shifted by 39 nm from that of **2** (λ_{max} = 507 nm) (Fig. 2b).

Metallapentalenoxazetes such as **3** and **4** possess a scaffold similar to that in cyclobutametallapentalenes (**V**, λ_{max} = 672 nm),[13] except for the different atoms in the fused four-membered ring. Interestingly, when the fused metallaoxazete unit was changed to the metallabutadiene unit, it resulted in a significant red-shift of the absorption maximum (>159 nm).

We further investigated the electrochemical properties of these metallapentalenoxazetes in acetonitrile by cyclic voltammetry (CV) with a glassy carbon as the working electrode, platinum rod as the auxiliary electrode, Ag/AgCl as the reference electrode, $[Bu_4N]PF_6$ as the supporting electrolyte, and a ferrocene/ferrocenium couple as the external standard. As shown in Fig. 2c, both **2** and **3** showed a reversible oxidation couple at half-wave potentials ($E_{1/2}$) of 1.18 V and 1.12 V, respectively, whereas two reversible oxidation waves were observed with an $E_{1/2}$ of 1.03 and 0.79 V for **4**. The dramatic cathodic shift of the first oxidation potential from 1.18 V for **2** to 0.79 V for **4** arises from the increasing HOMO levels from −7.15 eV to −6.52 eV (Table S1, ESI†), indicating that substituents at the *para*-position of the benzene ring have an obvious effect on the electrochemical behaviour. The first reduction potential onsets of **2–4** are slightly shifted from −0.97 V for **2** to −1.07 V for **4**, and are consistent with the LUMO levels of **2–4** that range from −4.21 to −4.02 eV. As for **6**, the introduction of a fused cyclopentene unit into the metallacycle framework resulted in a simultaneous cathodic shift of the first oxidation potential onsets (0.94 V) and the first reduction potential onsets (−1.16 V) (Fig. 2d). Thus, the results are consistent with the computational results and the absorption spectra. The high stability and low LUMO levels of the first metallapentalenoxazetes make them promising candidates as electron-acceptors in organic solar cells.[23]

In summary, this work demonstrates a cycloaddition reaction of metallapentalynes with nitrosoarenes (Ar–N═O). This is a new route to conjugated metallacycles and is also the first [2+2] cycloaddition reaction of the carbyne unit in metallapentalyne with double bond containing substrates. The photophysical properties of these compounds suggest that conversion of carbon atoms on metallacycle frameworks into nitrogen or oxygen atoms is a promising strategy to tune the photophysical properties. This study enriches the cycloaddition chemistry of metal carbynes and the metalla-aromatic chemistry.

This work was supported by the National Natural Science Foundation of China (No. 21772160, 21572185, and 21332002).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For selected reviews of metallabenzenes, see: (*a*) B. J. Frogley and L. J. Wright, *Chem. – Eur. J.*, 2018, **24**, 2025–2038; (*b*) B. J. Frogley and L. J. Wright, *Coord. Chem. Rev.*, 2014, **270–271**, 151–166; (*c*) M. Paneque, M. L. Poveda and N. Rendjn, *Eur. J. Inorg. Chem.*, 2011, 19–33; (*d*) C. W. Landorf and M. M. Haley, *Angew. Chem., Int. Ed.*, 2006, **45**, 3914–3936; (*e*) L. J. Wright, *Dalton Trans.*, 2006, 1821–1827; (*f*) G. He, H. Xia and G. Jia, *Chin. Sci. Bull.*, 2004, **49**, 1891–1899.

2 See for examples: (*a*) B. J. Frogley, L. C. Perera and L. J. Wright, *Chem. – Eur. J.*, 2018, **24**, 4304–4309; (*b*) Y. García-Rodeja and I. Fernández, *Chem. – Eur. J.*, 2017, **23**, 6634–6642; (*c*) B. J. Frogley and L. J. Wright, *Angew. Chem., Int. Ed.*, 2017, **56**, 143–147; (*d*) R. Lin,

K. H. Lee, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Organometallics*, 2015, **34**, 167–176; (*e*) Á. Vivancos, Y. Hernández, M. Paneque, M. L. Poveda, V. Salazar and E. Álvarez, *Organometallics*, 2015, **34**, 177–188; (*f*) Á. Vivancos, M. Paneque, M. L. Poveda and E. Álvarez, *Angew. Chem., Int. Ed.*, 2013, **52**, 10068–10071; (*g*) G. R. Clark, L. A. Ferguson, A. E. Mclntosh, T. Sohnel and L. J. Wright, *J. Am. Chem. Soc.*, 2010, **132**, 13443–13452; (*h*) V. Jacob, C. W. Landorf, L. N. Zakharov, T. J. R. Weakley and M. M. Haley, *Organometallics*, 2009, **28**, 5183–5190; (*i*) 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; (*j*) V. Jacob, T. J. R. Weakley and M. M. Haley, *Angew. Chem., Int. Ed.*, 2002, **41**, 3470–3473; (*k*) R. D. Gilbertson, T. J. R. Weakley and M. M. Haley, *Chem. – Eur. J.*, 2000, **6**, 437–441; (*l*) R. D. Gilbertson, T. J. R. Weakley and M. M. Haley, *J. Am. Chem. Soc.*, 1999, **121**, 2597–2598; (*m*) G. P. Elliott, W. R. Roper and J. M. Waters, *J. Chem. Soc., Chem. Commun.*, 1982, 811–813.

3 For selected reviews of metallabenzynes, see: (*a*) G. Jia, *Organometallics*, 2013, **32**, 6852–6866; (*b*) J. Chen and G. Jia, *Coord. Chem. Rev.*, 2013, **257**, 2491–2521; (*c*) J. Chen, G. He and G. Jia, *Chin. J. Org. Chem.*, 2013, **33**, 792–798.

4 See for examples: (*a*) W. Ruan, T. F. Leung, C. Shi, K. H. Lee, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Chem. Sci.*, 2018, **9**, 5994–5998; (*b*) T. B. Wen, K. H. Lee, J. Chen, W. Y. Hung, W. Bai, H. Li, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Organometallics*, 2016, **35**, 1514–1525; (*c*) J. Chen, K. H. Lee, T. B. Wen, F. Gao, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Organometallics*, 2015, **34**, 890–896; (*d*) J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Chem. – Eur. J.*, 2012, **18**, 14128–14139; (*e*) J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Angew. Chem., Int. Ed.*, 2011, **50**, 7295–7299; (*f*) J. Chen, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Angew. Chem., Int. Ed.*, 2011, **50**, 10675–10678.

5 For selected examples of metallaannulenes, see: (*a*) S. Zheng, Z. Chu, K.-H. Lee, Q. Lin, Y. Li, G. He, J. Chen and G. Jia, *ChemPlusChem*, 2019, **84**, 85–91; (*b*) J. Chen, K. H. Lee, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Angew. Chem., Int. Ed.*, 2016, **55**, 7194–7198; (*c*) J. Wei, Y. Zhang, Y. Chi, L. Liu, W. X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2016, **138**, 60–63.

6 See for examples: (*a*) M. Cui, R. Lin and G. Jia, *Chem. – Asian J.*, 2018, **13**, 895–912; (*b*) W. Ma, C. Yu, T. Chen, L. Xu, W. Zhang and Z. Xi, *Chem. Soc. Rev.*, 2017, **46**, 1160–1192; (*c*) P. Barrio, M. A. Esteruelas and E. Oñate, *J. Am. Chem. Soc.*, 2004, **126**, 1946–1947; (*d*) H. Wang, X. Zhou and H. Xia, *Chin. J. Chem.*, 2018, **36**, 93–105; (*e*) Q. Zhu, C. Zhu, Z. Deng, G. He, J. Chen, J. Zhu and H. Xia, *Chin. J. Chem.*, 2016, **34**, 628–634.

7 (*a*) 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 and H. Xia, *Nat. Chem.*, 2013, **5**, 698–703; (*b*) Q. Zhuo, J. Lin, Y. Hua, X. Zhou, Y. Shao, S. Chen, Z. Chen, J. Zhu, H. Zhang and H. Xia, *Nat. Commun.*, 2017, **8**, 1912.

8 (*a*) M. Mauksch and S. B. Tsogoeva, *Chem. – Eur. J.*, 2010, **16**, 7843–7851; (*b*) Y. Hua, H. Zhang and H. Xia, *Chin. J. Org. Chem.*, 2018, **38**, 11–28.

9 (*a*) C. Zhu and H. Xia, *Acc. Chem. Res.*, 2018, **51**, 1691–1700; (*b*) H. Xia, *Chin. J. Chem.*, 2018, **36**, 78; (*c*) Z. Lu, J. Chen and H. Xia, *Chin. J. Org. Chem.*, 2017, **37**, 1181–1188.

10 Z. Lu, C. Zhu, Y. Cai, J. Zhu, Y. Hua, Z. Chen, J. Chen and H. Xia, *Chem. – Eur. J.*, 2017, **23**, 6426–6431.

11 C. Zhu, J. Zhu, X. Zhou, Q. Zhu, Y. Yang, T. B. Wen and H. Xia, *Angew. Chem., Int. Ed.*, 2018, **57**, 3154–3157.

12 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.

13 C. Zhu, Y. Yang, M. Luo, C. Yang, J. Wu, L. Chen, G. Liu, T. Wen, J. Zhu and H. Xia, *Angew. Chem., Int. Ed.*, 2015, **54**, 6181–6185.

14 C. Zhu, Y. Yang, J. Wu, M. Luo, J. Fan, J. Zhu and H. Xia, *Angew. Chem., Int. Ed.*, 2015, **54**, 7189–7192.

15 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.

16 (*a*) Z. Lu, Q. Lin, Y. Cai, S. Chen, J. Chen, W. Wu, X. He and H. Xia, *ACS Macro Lett.*, 2018, **7**, 1034–1038; (*b*) Q. Lin, S. Li, J. Lin, M. Chen, Z. Lu, C. Tang, Z. Chen, X. He, J. Chen and H. Xia, *Chem. – Eur. J.*, 2018, **24**, 8375–8381; (*c*) Z. Lu, Y. Cai, Y. Wei, Q. Lin, J. Chen, X. He, S. Li, W. Wu and H. Xia, *Polym. Chem.*, 2018, **9**, 2092–2100; (*d*) X. He, X. He, S. Li, K. Zhuo, W. Qin, S. Dong, J. Chen, L. Ren, G. Liu and H. Xia, *Polym. Chem.*, 2017, **8**, 3674–3678; (*e*) C. Zhu, C. Yang, Y. Wang, G. Lin, Y. Yang, X. Wang, J. Zhu, X. Chen, X. Lu, G. Liu and H. Xia, *Sci. Adv.*, 2016, **2**, e1601031.

17 See for examples: (*a*) Q. Zhuo, H. Zhang, Y. Hua, H. Kang, X. Zhou, X. Lin, Z. Chen, J. Lin, K. Zhuo and H. Xia, *Sci. Adv.*, 2018, **4**, eaat0336; (*b*) J. Chen, Q. Lin, S. Li, Z. Lu, J. Lin, Z. Chen and H. Xia, *Organometallics*, 2018, **37**, 618–623; (*c*) C. Zhu, J. Wu, S. Li, Y. Yang, J. Zhu, X. Lu and H. Xia, *Angew. Chem., Int. Ed.*, 2017, **56**, 9067–9071; (*d*) C. Zhu, X. Zhou, H. Xing, K. An, J. Zhu and H. Xia, *Angew. Chem., Int. Ed.*, 2015, **54**, 3102–3106; (*e*) C. Zhu, M. Luo, Q. Zhu, J. Zhu, P. v. R. Schleyer, J. I. Wu, X. Lu and H. Xia, *Nat. Commun.*, 2014, **5**, 3265; (*f*) C. Zhu, Q. Zhu, J. Fan, J. Zhu, X. He, X. Y. Cao and H. Xia, *Angew. Chem., Int. Ed.*, 2014, **53**, 6232–6236.

18 (*a*) L. Gong, Y. Lin, T. Wen and H. Xia, *Organometallics*, 2009, **28**, 1101–1111; (*b*) G. He, J. Chen and H. Xia, *Sci. Bull.*, 2016, **61**, 430–442.

19 (*a*) V. K. Wieser and A. Berndt, *Angew. Chem.*, 1975, **87**, 73–74; (*b*) T. Bally, S. Chai, M. Neuenschwander and Z. Zhu, *J. Am. Chem. Soc.*, 1997, **119**, 1869–1875.

20 B. M. Handwerker, K. E. Garrett and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1989, **111**, 369–371.

21 See for examples: (*a*) *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003, vol. 1–3; (*b*) H. Ehrhorn and M. Tamm, *Chem. – Eur. J.*, 2019, **25**, 3190–3208; (*c*) D. P. Estes, C. P. Gordon, A. Fedorov, W. C. Liao, H. Ehrhorn, C. Bittner, M. L. Zier, D. Bockfeld, K. W. Chan, O. Eisenstein, C. Raynaud, M. Tamm and C. Coperet, *J. Am. Chem. Soc.*, 2017, **139**, 17597–17607; (*d*) D. P. Estes, C. Bittner, O. Arias, M. Casey, A. Fedorov, M. Tamm and C. Coperet, *Angew. Chem., Int. Ed.*, 2016, **55**, 13960–13964; (*e*) S. Schaubach, K. Gebauer, F. Ungeheuer, L. Hoffmeister, M. K. Ilg, C. Wirtz and A. Fürstner, *Chem. – Eur. J.*, 2016, **22**, 8494–8507; (*f*) A. Fürstner, *Angew. Chem., Int. Ed.*, 2013, **52**, 2794–2819.

22 See for examples: (*a*) S. S. Nadif, T. Kubo, S. A. Gonsales, S. VenkatRamani, I. Ghiviriga, B. S. Sumerlin and A. S. Veige, *J. Am. Chem. Soc.*, 2016, **138**, 6408–6411; (*b*) K. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 359–360; (*c*) B. M. Handwerker, K. E. Garrett, K. L. Nagle and G. L. Geoffroy, *Organometallics*, 1990, **9**, 1562–1575.

23 (*a*) A. Wadsworth, M. Moser, A. Marks, M. S. Little, N. Gasparini, C. J. Brabec, D. Baran and I. McCulloch, *Chem. Soc. Rev.*, 2019, **48**, 1596–1625; (*b*) J. E. Anthony, *Chem. Mater.*, 2011, **23**, 583–590.