

# Reactions of Isocyanides with Metal Carbyne Complexes: Isolation and Characterization of Metallacyclopropenimine Intermediates

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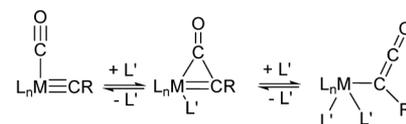
## Supporting Information

**ABSTRACT:**  $\eta^2$ -Iminoketenyl species have often been postulated as the intermediates in nucleophile-induced carbyne–isocyanide C–C coupling processes. However, such species are elusive. Here we report direct formation of  $\eta^2$ -iminoketenyl complexes from reactions of metallapentalyne with isocyanides. Our studies show that steric effects of N-substituents of the isocyanides play an important role in the stability of the three-membered metallacycles of the  $\eta^2$ -iminoketenyl complexes. Sterically bulky isocyanides, such as *tert*-butyl or 1-adamantyl isocyanides, inhibit bending at the isocyanide nitrogen atoms, a requirement for formation of  $\eta^2$ -iminoketenyl structures. Reactions of metallapentalyne with excess isocyanide allow the metal-bridged metallaindene derivative to be isolated as a result of the isocyanide insertion into the M–C <sub>$\alpha$</sub>   $\sigma$  bond of metallapentalyne.

Isocyanides have been recognized as versatile building blocks in a variety of metal-mediated and metal-catalyzed organic syntheses, enabling efficient transformation to elaborate organic structures.<sup>1</sup> Most examples of metal-mediated and/or metal-catalyzed reactions of isocyanide species involve the insertion of an isocyanide molecule into a metal–element bond.<sup>2</sup> C–C couplings involving coordinated isocyanide ligands have long been known,<sup>3,4</sup> which are similar to those well-established reductive C–C couplings involving isoelectronic carbonyls.<sup>5</sup> However, couplings involving coordinated isocyanide ligands are observed much less often, and almost all of the literature examples date back to the 1970–1990s.<sup>3</sup> As shown in Scheme 1, the crucial steps for reductive coupling involving carbonyl ligands are the nucleophile-induced carbyne–carbonyl coupling process. Even though the resulting  $\eta^2$ -ketenyl-metal intermediates in this process have been heralded for a long time,<sup>6</sup> isolation of such intermediates with  $\eta^2$ -iminoketenyl ligands appears to be unknown so far,<sup>7</sup> likely due to the fact that iminoketenyl ligands exhibit little  $\pi$ -accepting properties and prefer to be bonded to a metal center only via one carbon atom. Recently, a related and interesting heterocoupling between a borylenel ligand and a carbonyl ligand was reported,<sup>8</sup> which is similar to the carbyne–carbonyl coupling described above.

## Scheme 1. Formation of $\eta^2$ -Ketenyl-Metal and $\eta^2$ -Iminoketenyl-Metal Complexes

Metal carbyne–carbonyl coupling reactions



This work



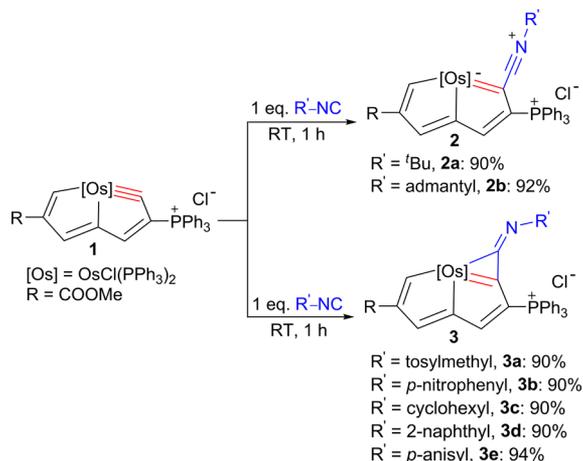
In our efforts to design metalla-aromatic systems that are metallacycles with aromaticity,<sup>9</sup> we have been investigating the chemistry of metallapentalynes, containing metal–carbon triple bonds within a five-membered ring.<sup>10</sup> While we have found that a metallapentalyne behaves as an aromatic molecule, we hypothesized that the carbyne moiety would exhibit unique reactivities and thereby offer unparalleled scope and versatility, particularly with respect to the isolation of some important intermediates. Very recently, we reported the halogenation of the metallapentalyne, from which we isolated the metallaiodirenium and metallabromirenium ions.<sup>11</sup> Herein, we describe the reactions of metallapentalyne with isocyanides that lead to the isolation of  $\eta^2$ -iminoketenyl metallapentalene intermediates as well as the unprecedented metallaindene derivatives. These complexes are likely to be formed through the direct attack of a free isocyanide on the carbyne carbon atom of the metallapentalyne. Our mechanistic studies also identify conditions under which these C–C coupling and insertion steps are experimentally observed.

As shown in Scheme 2, treatment of dichloromethane solutions of the osmapentalyne **1** with 1 equiv of *tert*-butyl isocyanide (*t*-BuNC) or 1-adamantyl isocyanide leads to the formation of complex **2a** or **2b**, both of which were isolated as brown solids in high yields. The presence of a *tert*-butyl isocyanide or 1-adamantyl isocyanide substituent at the  $\alpha$ -

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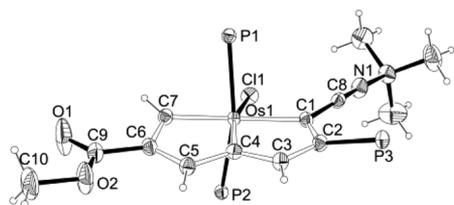
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## Scheme 2. Reactions of Osmapentalene with Isocyanides



carbon in **2** is strongly supported by NMR spectra. The singlets at 1.13 ppm in the <sup>1</sup>H NMR spectrum and at 142.5, 59.2, and 33.5 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, respectively, are characteristic features of the *tert*-butyl isocyanide structure in **2a**. In agreement with the adamantanyl isocyanide structure in **2b**, the carbons resonate at  $\delta$  58.9, 46.0, 34.9, and 29.2 ppm, and the adamantanyl protons give signals at  $\delta$  1.99–1.41 ppm. Note that the resonance corresponding to the OsCH proton appears at very low field, 34.46 (**2a**) and 34.07 (**2b**) ppm, different from our previously reported osmapentalenes.<sup>10,11</sup> Similar low-field chemical shifts of OsCH (48.01 ppm) were observed in our previously reported osmapyridine complex, which were attributed to partial paramagnetism.<sup>12</sup> The magnetic measurement experiments show temperature-dependent magnetic susceptibilities for **2a** and **2b** (Supporting Information (SI), Figure S1–S11), comparable to those reported for the osmapyridine complex.<sup>12</sup>

The structure of the cationic part of **2a** was determined by X-ray diffraction analysis of complex **2a'**, i.e., the derivative of **2a** featuring a different counteranion (details in section 2 of the SI). The X-ray diffraction study confirmed the nucleophilic addition of *tert*-butyl isocyanide and the formation of the substituted osmapentalene complex (Figure 1). The C8–N1

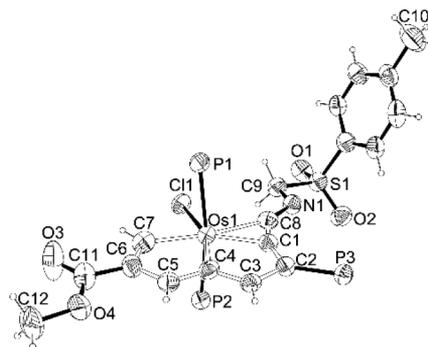


**Figure 1.** Solid-state structure of the cationic part of **2a'**. Thermal ellipsoids are set at the 50% probability level. Phenyl groups in PPh<sub>3</sub> ligands are omitted for clarity.

distance was determined to be 1.150(4) Å, which is short and agrees with the standard value for a triple bond. The C1–C8–N1 angle of 169.9(3)° is consistent with the nearly linear nature at C8 of the *tert*-butyl isocyanide substituent.

Using other substituted isocyanides under the same reaction conditions, we observed different products (Scheme 2). Treatment of **1** with equivalent tosylmethyl isocyanide in dichloromethane for 1 h provided **3a** in 90% yield. The reaction was also effective to generate analogue **3b** in 90% yield by

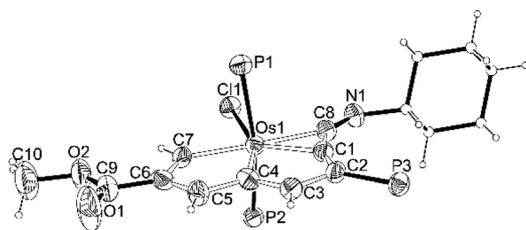
adding *p*-nitrophenyl isocyanide to the solution of **1**. The identity of these products was characterized on the basis of NMR spectral data and elemental analysis. In comparison to *t*-BuNC, these two isocyanides form the interesting  $\eta^2$ -iminoketenyl complexes, as confirmed by the crystal structure of **3a**. As shown in Figure 2, the structure of the fused



**Figure 2.** Solid-state structure of the cationic part of **3a**. Thermal ellipsoids are set at the 50% probability level. Phenyl groups in the PPh<sub>3</sub> ligands are omitted for clarity.

osmapentalene complex **3a** indicates that the iminoketenyl ligand coordinates to the osmium center in an  $\eta^2$  manner (Os1–C8 = 2.155(7) Å and Os1–C1 = 1.997(7) Å), thus forming a three-membered metallacycle. The C8–N1 distance of **3a** (1.264(8) Å) is obviously longer than that of **2**, indicating double bond character. The C1–C8–N1 angle in **3a** is 120.6°, which deviates remarkably from linearity. The metal center of **3a** serves as a common vertex for three metallacycles (the bicyclic metallapentalene unit and the fused three-membered metallacyclopropenimine unit). A comparable fused metallapentalene has been recently reported, which also contains a three-membered metallacyclopropene unit with an sp<sup>3</sup> carbon.<sup>10c</sup> Notably, the nine ring atoms (Os1 and C1–C8) of the fused osmapentalene ring in **3a** are coplanar, reflected by their very small mean deviation (0.0149 Å) from the least-squares plane. The metal–carbon bond distances are close to each other, except for the appreciably long Os1–C8 bond (2.155(7) Å). The carbon–carbon bond lengths (1.369(9)–1.413(9) Å) in the tricyclic skeleton are between typical single and double carbon–carbon bond lengths, which suggests the  $\pi$ -electron delocalization within the fused metallacycle.

In the search for more complexes with a metallacyclopropenimine unit, we also treated complex **1** with other isocyanides, such as cyclohexyl isocyanide, 2-naphthyl isocyanide, and *p*-anisyl isocyanide. As shown in Scheme 2, similar reactions took place, and the desired metallacyclopropenimine complexes **3c**, **3d**, and **3e** were isolated in high yields, respectively. These complexes were identified by NMR and elemental analysis (details in section 2 of the SI), and the  $\eta^2$ -iminoketenyl structure **3c** was also characterized by X-ray diffraction analysis (Figure 3). It is interesting to note that the cyclohexyl group in **3c**, in a *syn*-arrangement, points toward the phosphonium group on the metallacycle, which is different from the *anti*-arrangement in **3a**. The isocyanide group in **3c** gives a <sup>13</sup>C NMR signal at  $\delta$  143.1 ppm, significantly upfield-shifted when compared to the signals for the isocyanide groups on other metallacyclopropenimine complexes **3** (159.6–175.2 ppm) but very close to the values (142.4 and 142.6 ppm) observed for complexes **2**. The NMR results suggest that the isomeric



**Figure 3.** Solid-state structure of the cationic part of **3c**. Thermal ellipsoids are set at the 50% probability level. Phenyl groups in the  $\text{PPh}_3$  ligands are omitted for clarity.

isocyanide-substituted carbene structure might be a dominant species for the complex in solution.

Complexes **3** represent the first isolated examples of  $\eta^2$ -iminoketenyl intermediates formed by a carbyne–isocyanide coupling process. Density functional theory (DFT) calculations were conducted to study the effect of the N-substituents of isocyanides on the relative stability of the  $\eta^2$ -iminoketenyl structures (**3**) versus the isocyanide-substituted carbene structures (**2**).<sup>12</sup>

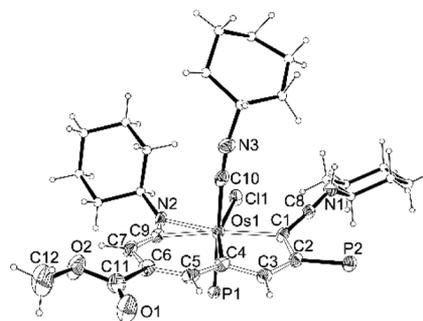
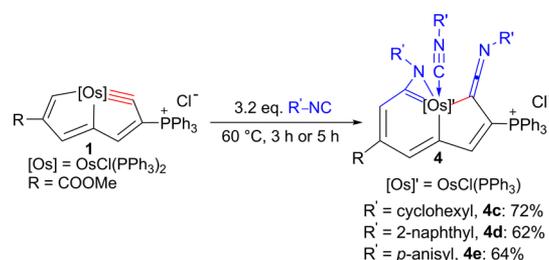
As discussed above, the N-substituents in **3** can adopt either an *anti*-arrangement (**3a**) or a *syn*-arrangement (**3c**) with respect to the phosphonium group on the metallacycle. Thus, both the *anti*- and *syn*-isomers for **3** were considered in our DFT calculations. The DFT results show that the *syn*-isomers are more stable than the *anti*-isomers for **3b**, **3c**, and **3d**. In contrast, the *anti*-isomer of **3a** is more stable than the *syn*-isomer by 19.3 kJ/mol, while the *syn*- and *anti*-isomers of **3e** are of similar stability. The *syn* or *anti* arrangement can be attributed to a subtle balance of the non-covalent interactions between the N-substituent and the phosphonium group on the metallacycle. However, the complexity of the non-covalent interaction prevents us from achieving a thorough understanding of the balance.

For complexes **2a** and **2b**, where the N-substituents are bulky *tert*-butyl and adamantanyl, the DFT results show that the carbene structures are indeed more stable than the  $\eta^2$ -iminoketenyl structures (see SI for detailed results). In sharp contrast, for complexes **3a–3e**, their isomeric carbene structures were calculated to be less stable than the experimentally observed  $\eta^2$ -iminoketenyl structures.<sup>13</sup> These DFT results are in good agreement with the experimental observations shown in Scheme 2. We reason that the sterically bulky N-substituents *tert*-butyl and 1-adamantyl impede the bending at the isocyanide nitrogen, preventing the formation of an  $\eta^2$ -iminoketenyl structure.

Interestingly, addition of excess cyclohexyl isocyanide, 2-naphthyl isocyanide, and *p*-anisyl isocyanide led to the insertion products, metallaindene derivatives **4c–4e**, respectively; in each of which, one isocyanide molecule is added as a ligand and another one inserts into an Os–C bond, resulting in expansion of the metallacyclic skeleton (Scheme 3). The molecular structure of **4c** is shown in Figure 4. Complexes **4** are the metallaindene derivatives, which represent a novel type of metal-bridged polycyclic metallaaromatics.

To further shed light on the aromatic nature of the new complexes, DFT calculations were carried out on the simplified unsubstituted model complexes **3'** and **4'**, where the  $\text{PH}_3$  ligands replace the  $\text{PPh}_3$  ligands and the methyl groups replace N-substituents.<sup>13</sup> It has been widely believed that negative nucleus-independent chemical shift (NICS)<sup>14</sup> values indicate aromaticity. Consistent with previously reported metalla-

### Scheme 3. Formation of Metal-Bridged Metallaindene Derivatives



**Figure 4.** Solid-state structure of the cationic part of **4c**. Thermal ellipsoids are set at the 50% probability level. Phenyl groups in  $\text{PPh}_3$  moieties are omitted for clarity.

aromatics, the calculated  $\text{NICS}(1)_{zz}$  values for the three metallacyclic rings of **3'** and **4'** are all negative (−10.2, −20.8, and −30.5 ppm for **3'**; −9.5, −3.8, and −30.0 ppm for **4'**).

In conclusion, we have presented that  $\eta^2$ -iminoketenyl complexes can be synthesized as isolable species through the reactions of metallapentalyne with isocyanides. NMR spectroscopy and crystallographic analysis confirmed the metallacyclopentadiene nature of the three-membered metallacycles, which could be regarded as the first isolated intermediates for the reductive coupling involving isocyanide ligands. In addition, we showed that further insertion of the isocyanide would allow access to the formation of the metallaindene derivatives, as a rare example of metallaaromatics with photoacoustic properties. Our combined experimental and computational studies demonstrated that the steric and electronic properties of the N-substituents are very important for the formation of the  $\eta^2$ -iminoketenyl complexes and the metallaindene derivatives.

### ■ ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13275.

Experimental procedures, characterization of compounds, and computational details (PDF)

Crystallographic data for **2**, **3a**, **3c**, and **4c** (CIF)

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Reviews: (a) Boyarskiy, V. P.; Bokach, N. A.; Luzyanin, K. V.; Kukushkin, V. Y. *Chem. Rev.* **2015**, *115*, 2698. (b) Zhang, B.; Studer, A. *Chem. Soc. Rev.* **2015**, *44*, 3505. (c) Vlaar, T.; Ruijter, E.; Maes, B. U. W.; Orru, R. V. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7084. (d) Qiu, G.; Ding, Q.; Wu, J. *Chem. Soc. Rev.* **2013**, *42*, 5257.
- (2) Selected examples of insertion reactions involving isocyanides: (a) Valadez, T. N.; Norton, J. R.; Neary, M. C. *J. Am. Chem. Soc.* **2015**, *137*, 10152. (b) Liu, J.; Liu, Z.; Liao, P.; Zhang, L.; Tu, T.; Bi, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 10618. (c) Geng, W.; Wei, J.; Zhang, W.-X.; Xi, Z. *J. Am. Chem. Soc.* **2014**, *136*, 610. (d) Xue, Y.-X.; Zhu, Y.-Y.; Gao, L.-M.; He, X.-Y.; Liu, N.; Zhang, W.-Y.; Yin, J.; Ding, Y.; Zhou, H.; Wu, Z.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 4706. (e) Zhang, S.; Zhang, W.-X.; Xi, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 3485. (f) Fukumoto, Y.; Hagihara, M.; Kinashi, F.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 10014. (g) Zhang, W.-X.; Zhang, S.; Sun, X.; Nishiura, M.; Hou, Z.; Xi, Z. *Angew. Chem.* **2009**, *121*, 7363.
- (3) (a) Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Michelin, R. A. *Coord. Chem. Rev.* **2001**, *218*, 43. (b) Rehder, D.; Bottcher, C.; Collazo, C.; Hedelt, R.; Schmidt, H. *J. Organomet. Chem.* **1999**, *585*, 294. (c) Kloppenburg, L.; Petersen, J. L. *Organometallics* **1997**, *16*, 3548. (d) Collazo, C.; Rodewald, D.; Schmidt, H.; Rehder, D. *Organometallics* **1996**, *15*, 4884. (e) Wang, Y.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A.; Henderson, R. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1995**, 1183. (f) Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L.; Frausto da Silva, J. J. R.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1995**, 1193. (g) Acho, J. A.; Lippard, S. J. *Organometallics* **1994**, *13*, 1294. (h) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90. (i) Mayr, A.; Holmes, S. M.; Bastos, C. M. *Organometallics* **1992**, *11*, 4358. (j) Filippou, A. C.; Völkl, C.; Grünleitner, W.; Kiprof, P. *J. Organomet. Chem.* **1992**, *434*, 201. (k) Filippou, A. C.; Grünleitner, W.; Völkl, C.; Kiprof, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1167. (l) Mayr, A.; Bastos, C. *J. Am. Chem. Soc.* **1990**, *112*, 7797. (m) Vrtis, R. N.; Rao, Ch. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669. (n) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (o) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263. (p) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617.
- (4) Recent examples of reductive C–C coupling involving isocyanides: (a) Kriegl, B. M.; Bergman, R. G.; Arnold, J. J. *Am. Chem. Soc.* **2016**, *138*, 52. (b) Shen, J.; Yap, G. P. A.; Theopold, K. H. *J. Am. Chem. Soc.* **2014**, *136*, 3382.
- (5) (a) Wayland, B.; Fu, X. *Science* **2006**, *311*, 790. (b) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281.
- (6) (a) Carnahan, E. M.; Rardin, R. L.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 5193. (b) Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 4166. (c) Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 3230. (d) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818. (e) Kreissl, F. R.; Reber, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 643. (f) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (g) Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476. (h) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Chem. Ber.* **1977**, *110*, 3782. (i) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632.
- (7) (a) Mayr, A.; Holmes, S. M.; Bastos, C. M. *Organometallics* **1992**, *11*, 4358. (b) Baker, P. K.; Barker, G. K.; Gill, D. S.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1321. (c) Gill, D. S.; Baker, P. K.; Green, M.; Paddick, K. E.; Murray, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 19, 986.
- (8) Braunschweig, H.; Radacki, K.; Shang, R.; Tate, C. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 729.
- (9) (a) Fernández, I.; Frenking, G.; Merino, G. *Chem. Soc. Rev.* **2015**, *44*, 6452. (b) Frogley, B. J.; Wright, L. J. *Coord. Chem. Rev.* **2014**, *270*, 151. (c) Cao, X.-Y.; Zhao, Q.; Lin, Z.; Xia, H. *Acc. Chem. Res.* **2014**, *47*, 341. (d) Chen, J.; Jia, G. *Coord. Chem. Rev.* **2013**, *257*, 2491.
- (10) (a) Zhu, C.; Yang, C.; Wang, Y.; Lin, G.; Yang, Y.; Wang, X.; Zhu, J.; Chen, X.; Lu, X.; Liu, G.; Xia, H. *Sci. Adv.* **2016**, *2*, e1601031. (b) Zhu, C.; Yang, Y.; Wu, J.; Luo, M.; Fan, J.; Zhu, J.; Xia, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 7189. (c) Zhu, C.; Yang, Y.; Luo, M.; Yang, C.; Wu, J.; Chen, L.; Liu, G.; Wen, T.; Zhu, J.; Xia, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 6181. (d) Zhu, C.; Zhou, X.; Xing, H.; An, K.; Zhu, J.; Xia, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 3102. (e) Zhu, C.; Zhu, Q.; Fan, J.; Zhu, J.; He, X.; Cao, X.-Y.; Xia, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 6232. (f) Zhu, C.; Luo, M.; Zhu, Q.; Zhu, J.; Schleyer, P. v. R.; Wu, J. I. C.; Lu, X.; Xia, H. *Nat. Commun.* **2014**, *5*, 3265. (g) Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T. B.; Xie, Z.; Schleyer, P. v. R.; Xia, H. *Nat. Chem.* **2013**, *5*, 698.
- (11) Luo, M.; Zhu, C.; Chen, L.; Zhang, H.; Xia, H. *Chem. Sci.* **2016**, *7*, 1815.
- (12) Liu, B.; Wang, H.; Xie, H.; Zeng, B.; Chen, J.; Tao, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5430.
- (13) Detailed DFT results are given in section 3 of the SI.
- (14) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.