Dalton Transactions

PAPER

Theoretical study on the stability of osmasilabenzynes†

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Metallabenzyne has attracted considerable interest from theoreticians and experimentalists since its first isolation in 2001. However, metallasilabenzyne, formed by the replacement of the carbyne carbon with a silicon atom in metallabenzyne, has never been reported either theoretically or experimentally. Here we carry out density functional theory (DFT) calculations on this system for the first time. Our results reveal a polarized and weak Os−Si triple bond in osmasilabenzyne due to the reluctance of the silicon to participate in π bonding. The effect of the ligands, substituents on the metallacycle, and bases on the stability or aromaticity of osmasilabenzyne is also discussed in detail. Specifically, an antibonding interaction between the metal and metal-bonded carbon and silicon in the HOMO of osmasilabenzyne is identified. Thus electron-donating substituents on the metallacycle can destabilize it. Because the Os−Si triple bond in osmasilabenzyne is highly polarized, a Lewis base can stabilize it by coordinating to the silicon atom. All these findings could be helpful for experimentalists to realize the first metallasilabenzyne.

Introduction

Benzyne, as an important intermediate in organic synthesis, has attracted considerable interest[1] since Roberts *et al.* tracked it by performing the classic ^{14}C labelling experiment in 1953.[1a] Nevertheless, it is difficult to isolate and shows high reactivity due to the large ring strain caused by the bent C≡C triple bond. Interestingly, metallabenzyne, formed by the formal replacement of one sp-hybridized carbon atom in benzyne with an isolobal transition metal fragment, has been synthesized and isolated by Jia's group in 2001.[2] Since then a dozen metallabenzynes have been realized.[3] The relatively high thermal stability of metallabenzyne over benzyne could be attributed to the reduced ring strain (9.6 *vs.* 51.8 kcal mol^{-1}) reported by Jia, Lin *et al.*[4] How about the stability of metallasilabenzynes, formed by the replacement of the carbyne carbon with a silicon atom in metallabenzyne? As smaller angle strain is expected by the larger atomic size, the stability could be enhanced.

benzyne 1953   metallabenzyne 2001   metallasilabenzyne ?
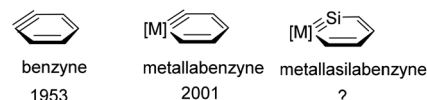
However, silicon is reluctant to participate in π bonding.[5] Thus, a transition metal silicon multiple bond is not easily formed because the low electronegativity of silicon leads to weak π bonds and high polarization of the metal–silicon bond. Therefore no X-ray structure of a transition metal silylene complex was reported until 1987.[6] For metal silylidyne complexes, only limited examples have been synthesized recently.[7] The polarization of a transition metal silicon multiple bond leads to high reactivities of these complexes toward nucleophiles, such as water, alcohols, ketones, isocyanates, and phosphorus ylides.[8] So high reactivities of metallasilabenzyne arising from the polarization of the metal–silicon triple bond are expected. When aromaticity is taken into account, how about the stability of metallasilabenzynes? To the best of our knowledge, there is no report on this system. Our ongoing interest in aromaticity has led us to investigate these metallasilaaromatics.[9] Here we present thorough density function theory (DFT) calculations on osmasilabenzynes. How the ligands, substituents on the metallacycle, and base affect the stability or aromaticity will be discussed in detail. We purposely chose osmasilabenzyne as our model complex because the first metallabenzene,[10] metallabenzyne,[2] and metallanaphthalyne[3f] were synthesized by osmium complexes.

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3dt53528b

Results and discussion

Osmium–silicon triple bond

As osmasilabenzyne could be regarded as a cyclic metal silyl-idyne complex, we therefore examine the Os–Si triple bond. In general, transition metal carbyne complexes can be classified as Fischer carbynes and Schrock carbynes.[11] The free carbyne can be considered as a doublet for the Fischer and quartet for the Schrock form. In Fischer carbynes, one p orbital on the carbyne carbon remains empty and is able to receive back donation from the filled M (dπ) orbital (Fig. 1) whereas the quartet carbyne in the Schrock form can form three covalent bonds to a metal. Most electron-rich late transition metal carbynes tend to form the Fischer type whereas most early ones favor the Schrock type. As late transition metal silylidynes have only limited cases which have been synthesized or isolated so far,[7e] we therefore designed a Fischer osmium silylidyne complex and compared it with the corresponding carbyne complex (Table 1).

According to the NBO analysis of complexes **1a** and **1b** (Table 1), the bond order of an osmium–silicon triple bond is only 1.71 which is much smaller than that of the osmium–carbon triple bond (2.13). In addition, the electron population of the Os–Si triple bond is 3.86, in sharp contrast with that of the Os–C triple bond (5.78), indicating a weaker osmium–silicon triple bond. The NBO charge on the silicon atom becomes positive, which contrasts sharply with the negative charge on the carbyne carbon, suggesting a weaker back donation from the osmium to the silicon atom and leading to a highly polarized Os–Si triple bond. All these data reveal a relatively weaker Os–Si triple bond, in line with the recent study on osmium silylidynes.[7e]
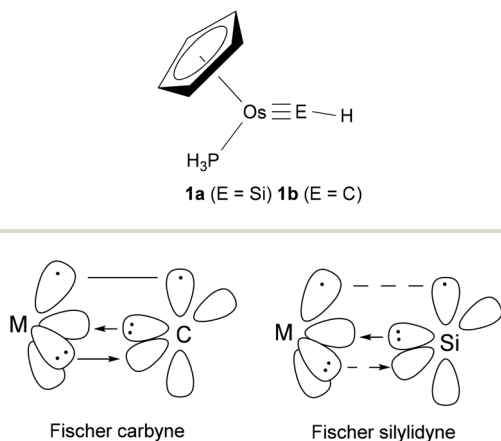
Geometric and electronic structure of osmasilabenzyne

According to the optimized structure, the metallacycle in **2a** is planar, which is indicated by the six particularly small dihedral angles (∠Os–Si–C1–C2 = 0°, ∠Si–C1–C2–C3 = 0.003°, ∠C1–C2–C3–C4 = −0.001°, ∠C2–C3–C4–Os = −0.006°, ∠C3–C4–Os–Si = 0.007°, ∠C4–Os–Si–C1 = −0.004°). The sum of the internal angles within the ring is 719.9°, very close to the ideal value of 720° required for a planar hexagon. Moreover, the Os–Si bond (2.190 Å) is shorter than those (2.22–2.26 Å) of the Os–Si double bond[12] and the Si–C, C–C, and Os–C bonds are intermediates between a single and double bond, suggesting aromaticity in osmasilabenzyne **2a**. The Os–Si bond in **2a** is slightly longer than that in **1a** possibly to reduce the ring strain caused by the nonlinear triple bond.

To evaluate the ring strain, we compared the energy difference between the partially and fully optimized complexes. In the partial optimization, the bond angle is fixed to 134.1°, which is exactly the same as that in **2a**. Indeed, the ring strain is reduced to 2.3 kcal mol^{-1}, which is smaller than that of osmabenzyne (9.6 kcal mol^{-1}), possibly due to the larger size of the silicon atom over the carbon atom. In addition, the ring strain in osmasilabenzyne was also calculated based on cyclic reference compounds via an isodesmic reaction[13] (Fig. 2b). Our calculations show that the ring strain is also as small as 1.5 kcal mol^{-1}, which is similar to that computed by the acyclic reference compound. It should be noted that even in the optimized structure in Fig. 2b, the bond angle at the silicon atom is 152.3°. A similar bent structure has been found in the first isolated disilyne.[14]

Similarly, the electron population of the Os–Si bond is 3.55 in **2a** whereas that of the Os–C bond in **2b** is 5.71 (Table 2). In
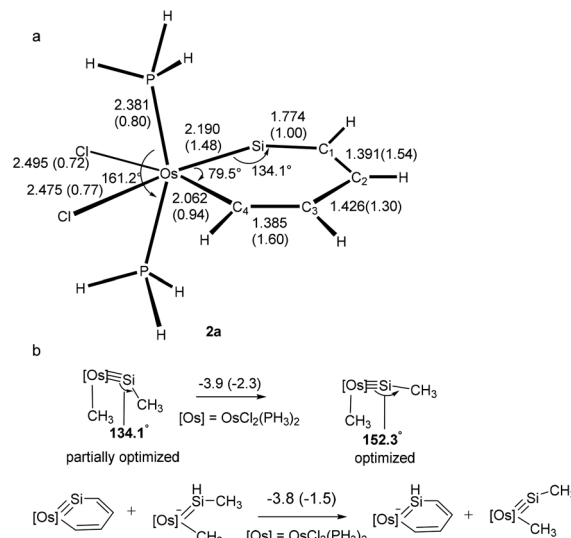

1a (E = Si) **1b** (E = C)

Fig. 1 Schematic diagram of a Fischer carbyne complex and Fischer silylidyne complex.

Table 1 The bond lengths, bond orders, charges, and electron populations of Os≡E bonds (E = Si or C) in **1a** and **1b**

E	Bond length (Å)	Bond order (Wiberg)	Charge (Os)	Charge (E)	Os–E bond pop. (electrons)
C	1.738	2.13	+0.04	−0.34	5.78
Si	2.157	1.71	−0.34	+0.43	3.86

Fig. 2 (a) The optimized structure with selected bond lengths (Å), bond angles (°), and bond orders given in parentheses by NBO calculations in osmasilabenzyne **2a**. (b) The calculated strain energy of osmasilabenzynes **2a** based on acyclic and cyclic reference compounds. The Gibbs free energies and relative electronic energies at 298 K (in parentheses) are given in kcal mol^{-1}.

Table 2 The bond lengths, bond orders, charges, and electron populations of Os≡E bonds (E = Si, or C) in **2a** and **2b**

Complex	Bond length (Å)	Bond order (Wiberg)	Charge (Os)	Charge (E)	Os≡E bond pop. (electrons)
2a	2.190	1.48	−1.60	+1.46	3.55
2b	1.775	1.63	+0.12	+0.14	5.71
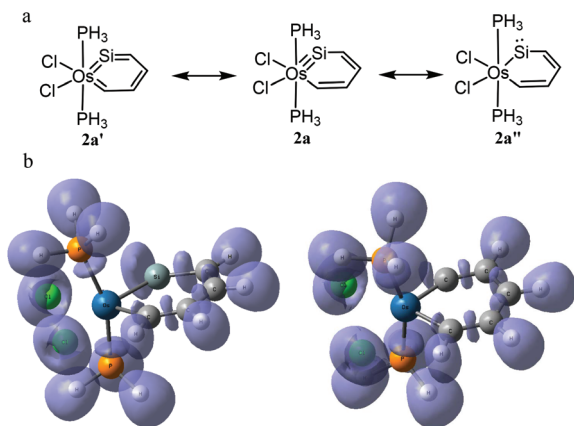
Fig. 3 (a) Resonance structures of osmasilabenzyne **2a**. (b) ELF iso-surfaces with isovalue = 0.85 in osmasilabenzyne **2a** (left) and osmabenzyne **2b** (right).

addition, the NBO charge on the silicon atom is much more positive than the carbyne carbon. Apparently, silicon is reluctant to participate in π bonding as we mentioned before,[5] leading to a weaker Os–Si triple bond compared with the Os–C triple bond. Such reluctance may also lead to some electrons in the lone-pair in **2a**. To test this hypothesis, we performed ELF calculations on osmasilabenzyne **2a** and compared it with the corresponding osmabenzyne **2b**. As shown in Fig. 3, the basin population on the carbyne carbon in osmabenzyne **2b** is small whereas it appears on the silicon atom in osmasilabenzyne **2a** associated with the lone pair character of silicon. Thus the aromaticity in **2a** should be reduced compared with that in **2b**.

The "isomerization stabilization energy" (ISE) method of Schleyer, and Zhu, which is particularly effective to probe the magnitude of aromatic π conjugation for highly strained systems in both the ground state[15] and lowest triplet state,[9e] was applied to evaluate the aromaticity in **2a** and **2b** as shown in Fig. 4. The indene–isoindene ISE approach is homodesmotic and has the advantage that all carbon atoms in the six-membered ring are sp²-hybridized in both the reactants and products. The uncorrected ISE value of **2a** is 10.1 kcal mol⁻¹, which is slightly smaller than that of **2b** and much smaller than that of benzene (21.8 kcal mol⁻¹)[15b] or osmapentalynes (19.6 kcal mol⁻¹).[9h]

To gain an insight into the aromaticity in **2a**, we performed canonical molecular orbital (CMO) nucleus-independent chemical shift (NICS)[16] calculations.[17] The four occupied out-of-plane π MOs of **2a** in Fig. 5 reflect the π delocalization along
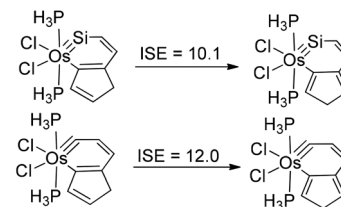
Fig. 4 Indene−isoindene ISE evaluations of the antiaromaticity of osmasilabenzyne **2a** and osmabenzyne **2b**. The energies (kcal mol⁻¹) include the zero-point energy corrections.
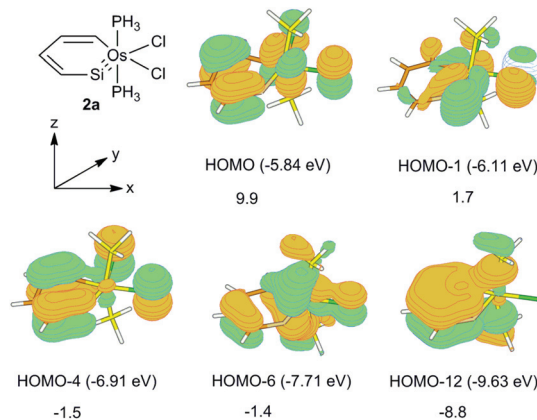
Fig. 5 NICS(1)$_{zz}$ contributions (ppm) of all the occupied π MOs of osmasilabenzyne **2a**. The eigenvalues of the MO's are given in parentheses.

the metallacycle. These four MO's are derived principally from the orbital interactions between the p$_{z\pi}$ atomic orbitals of the C_4SiH_4 unit and two of the d orbitals of the Os atom ($5d_{xz}$ and $5d_{yz}$). The HOMO described an antibonding interaction between the metal center and the metal-bonded carbon and silicon, similar to that of osmabenzyne.[4] The NICS(1)$_{zz}$ value in **2a** is −9.3 ppm. In general, negative values indicate aromaticity and positive values antiaromaticity. This NICS(1)$_{zz}$ value is less negative than that of benzyne (−33.0 ppm) or osmabenzyne (−15.0 ppm),[9h] further confirming that silicon is reluctant to participate in π bonding.[5]

Substituent effects on the stabilization of osmasilabenzyne

There is a great effect of substituents on the stabilization of metallabenzene[18] and metallabenzyne.[4] Thus it is expected that a substituent effect might exist in osmasilabenzynes. As there is an antibonding interaction between the metal center and the metal-bonded carbon and silicon in the HOMO of **2a**, we expect that electron-donating groups (EDGs) will destabilize **2a** as the antibonding interaction will be increased whereas electron-withdrawing groups (EWGs) will stabilize **2a** as such an antibonding interaction will be decreased. Indeed, the methoxyl substituent gives relatively smaller ISE values whereas the phosphonium leads to relatively larger ISE values (Fig. 6). According to MO theory, an EWG at the *meta* position will decrease the electron density more than at the *para*
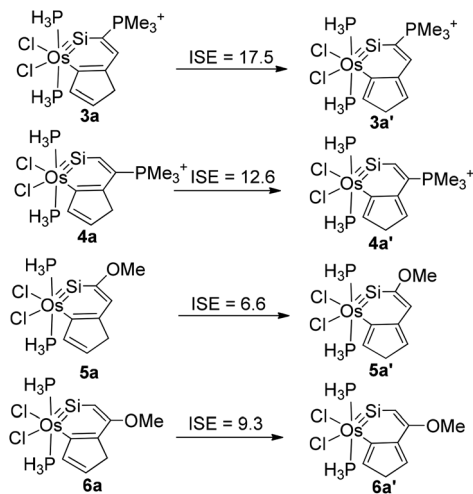
Fig. 6 Substituent effects on the stabilization of osmasilabenzyne **2a** evaluated by the ISE (kcal mol^{-1}) method.

position. Thus the stabilization of the EWG at the *meta* position becomes more significant than that at the *para* position. Similarly, the destabilization of an EDG at the *meta* position is also higher than at the *para* position.

Ligand effects on the stabilization of osmasilabenzyne

As EWGs on the metallacycle can stabilize osmasilabenzyne **2a**, electron-withdrawing ligands should also stabilize **2a** for the same reason. However, when the strong π-acceptor ligand CO was used to replace one of the chlorides in **2a**, destabilization was indicated by a smaller ISE value (5.0 kcal mol^{-1}). It is well-known that CO can significantly decrease the electron density of a metal center due to strong back-donation. Thus the antibonding in the HOMO of **2a** is decreased. However, decreasing the electron density of the metal center also weakens the bond strength of the metal–carbon on the metallacycle significantly. Specifically, when CO is used to replace one of the chlorides in **2a**, the Os–Si bond decreases from 2.190 to 2.183 Å (by 0.007 Å, 0.3%) whereas the Os–C bond increases from 2.062 to 2.174 Å (by 0.112 Å, 5.4%), respectively. Therefore, the conjugation decreases significantly, leading to reduced aromaticity, which is in line with the previous observation that the chloride is able to stabilize osmabenzyne.[19] Our previous study has shown that the cyclopentadienyl (Cp) ligand can change the antibonding interaction to a bonding interaction in metallabenzene by switching the HOMO.[20] Thus we also examined the effect of Cp and Ph ligands. Indeed, a bonding interaction dominates in the HOMOs of **9a** and **10a** (Fig. 8). The stabilization is supported by either a larger ISE value (Fig. 7) or more negative NICS(1)$_{zz}$ values (Fig. 8).

Lewis base effect on the stabilization for osmasilabenzyne

The first isolated silylene complex[6] benefited from a Lewis base because the M=Si double bond is highly polarized toward M$^{\delta-}$=Si$^{\delta+}$.[21] Therefore, it is expected that coordinating a base at the electron-deficient silicon atom could stabilize
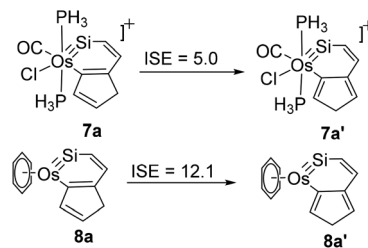

Fig. 7 Ligand effects on the stabilization of osmasilabenzyne **2a** evaluated by the ISE (kcal mol^{-1}) method.
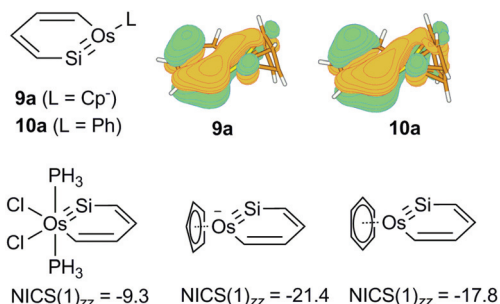

Fig. 8 HOMOs and NICS(1)$_{zz}$ (ppm) of **9a** with the Cp ligand and **10a** with the benzene ligand.
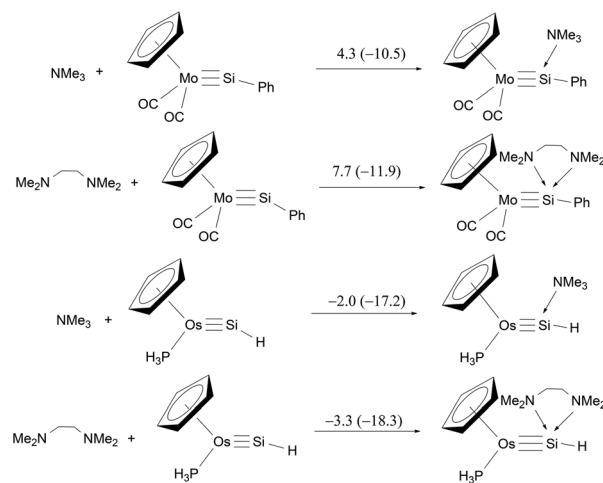

Fig. 9 Thermodynamic stabilities of silylidyne complexes containing a Lewis base at the silicon atom. The relative Gibbs free energies at 298 K and electronic energies (in parentheses) are given in kcal mol^{-1}.

metal silylene complexes. As shown in Table 1, the Os≡Si bond is also polarized. Accordingly, stabilization by a Lewis base is expected. Indeed, as shown in Fig. 9, bases can stabilize Fischer osmium silylidyne **1a** although the magnitude of the stabilization is weak. Interestingly, the base stabilization disappears for early transition metal silylidyne. This is understandable as the Schrock silylidyne could be assigned to these silylidynes. Thus the silicon is not electron-deficient.

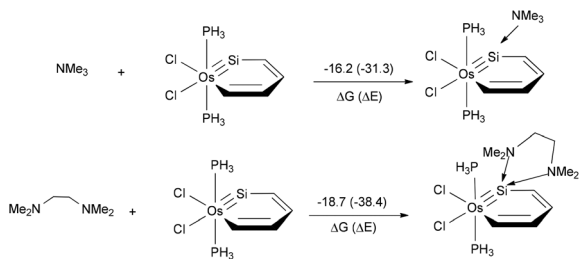We then examined the base effect on osmasilabenzyne as shown in Fig. 10. The monodentate base trimethylamine gives

Fig. 10 Thermodynamic stabilities of osmasilabenzyne coordinating a Lewis base on silicon. The Gibbs free energies and relative electronic energies at 298 K (in parentheses) are given in kcal mol^{-1}.
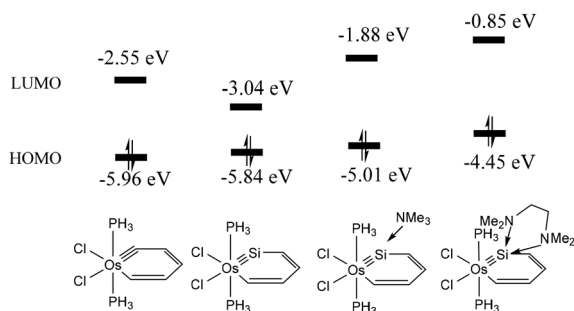

Fig. 11 The energy of selected frontier molecular orbitals (HOMO and LUMO) of osmabenzyne **2b**, osmasilabenzyne **2a**, and base-coordinated **2a**.

similar results to the bidentate base tetramethylethane-1,2-diamine. Interestingly, the stabilization of Lewis bases on osmasilabenzyne **2a** is much stronger than osmium silylidyne **1a**. NBO analysis on **2a** reveals that the polarization of Os≡Si becomes significant indicated by the more positive charge (1.46) on the silicon atom, leading to high stabilization caused by coordinating the base. Such stabilization is also supported by their low-lying LUMOs as shown in Fig. 11. According to the MO analysis, osmasilabenzyne **2a** has a lower LUMO than osmabenzyne **2b**, leading to a better energy match for the HOMO of the nucleophiles. Thus **2a** becomes unstable towards nucleophiles. This could be one of the reasons why metallasilabenzyne has never been synthesized. When the bases are coordinated to the silicon atom, their LUMOs become higher in energy, leading to stabilization.

Conclusions

In summary, DFT calculations have been performed to examine the stability of osmasilabenzyne. The ring strain was estimated to be almost negligible. Due to the reluctance of the silicon to participate in π bonding, the aromaticity of osmasila-benzyne is weaker than that of osmabenzyne. An antibonding interaction between the metal and metal-bonded carbon and silicon in the HOMO of osmasilabenzyne is identified. Thus

EWGs on the metallacycle can stabilize it. Because the Os≡Si bond in osmasilabenzyne is highly polarized, a Lewis base can also stabilize it by coordinating to the silicon atom. All these findings could be helpful for experimentalists to realize metallasilabenzynes.

Experimental section

Computational details

The B3LYP level[22] of density functional theory was used to optimize all of the structures studied in this work. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency). The LanL2DZ basis set was employed to describe Os, Si, P, Cl whereas the standard 6-31G(d) basis set was used for all other atoms. Polarization functionals were added for P (ζ(d) = 0.340), Cl (ζ(d) = 0.514), Si (ζ(d) = 0.262), Os (ζ(f) = 0.886).[23] To examine the effect of basis sets, we employed a larger 6-311+G(d,p) basis set[24] to optimize the structures in Fig. 4. The ISE values of **2a** and **2b** are 9.9 and 11.7 kcal mol^{-1}, respectively, which are very close to those (10.1 and 12.0 kcal mol^{-1}) using the 6-31G(d) basis set. To examine the functional dependence, we also optimized all the complexes in Fig. 4. The ISE values of **2a** and **2b** at the M06/6-311+G(d,p) level[25] are 9.8 and 10.9 kcal mol^{-1}, respectively. Moreover, the ISE values of **2a** and **2b** at the B97D/6-31G(d) level[26] are 10.4 and 11.6 kcal mol^{-1}, respectively. All these results indicate that the effects of basis set and functional are particularly small. The data of M06 and B97D were calculated by the Gaussian 09 package[27] whereas other calculations were carried out using the Gaussian 03 package.[28] To gain a proper understanding of the chemical bonding, NBO (natural bond orbital analysis)[29] and ELF (electron localization function)[30] methods were employed.

Acknowledgements

Notes and references

1 (*a*) J. D. Roberts, H. E. Simmons Jr., L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, 1953, **75**, 3290–3291; (*b*) J. D. Roberts, D. A. Semenow, H. E. Simmons Jr. and L. A. Carlsmith, *J. Am. Chem. Soc.*, 1956, **78**, 601–611; (*c*) J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and

D. A. Semenow, *J. Am. Chem. Soc.*, 1956, **78**, 611–614; (*d*) H. Heaney, *Chem. Rev.*, 1962, **62**, 81–97.

2 T. Wen, Z. Zhou and G. Jia, *Angew. Chem., Int. Ed.*, 2001, **40**, 1951–1954.

3 (*a*) T. Wen, W. Hung, H. H. Y. Sung, I. D. Williams and G. Jia, *J. Am. Chem. Soc.*, 2005, **127**, 2856–2857; (*b*) G. Jia, *Coord. Chem. Rev.*, 2007, **251**, 2167–2187; (*c*) T. Wang, H. Zhang, F. Han, R. Lin, Z. Lin and H. Xia, *Angew. Chem., Int. Ed.*, 2012, **51**, 9838–9841; (*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*) Q. Zhao, J. Zhu, Z. Huang, X. Cao and H. Xia, *Chem. - Eur. J.*, 2012, **18**, 11597–11603; (*f*) G. He, J. Zhu, W. Hung, T. Wen, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Angew. Chem., Int. Ed.*, 2007, **46**, 9065–9068; (*g*) B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. Wen, Z. Cao and H. Xia, *Angew. Chem., Int. Ed.*, 2009, **48**, 5461–5464; (*h*) J. Chen, H. H. Y. Sung, I. D. Williams, Z. Lin and G. Jia, *Angew. Chem., Int. Ed.*, 2011, **50**, 10675–10678; (*i*) J. Chen and G. Jia, *Coord. Chem. Rev.*, 2013, **257**, 2491–2521; (*j*) X. Cao, Q. Zhao, Z. Lin and H. Xia, *Acc. Chem. Res.*, 2014, **47**, 341–354; (*k*) G. Jia, *Organometallics*, 2013, **32**, 6852–6566.

4 S. M. Ng, X. Huang, T. Wen, G. Jia and Z. Lin, *Organometallics*, 2003, **22**, 3898–3904.

5 W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 272–295.

6 (*a*) C. Zybill and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 669–670; (*b*) D. A. Straus and T. D. Tilley, *J. Am. Chem. Soc.*, 1987, **109**, 5872–5873.

7 (*a*) S. D. Grumbine, R. K. Chadha and T. D. Tilley, *J. Am. Chem. Soc.*, 1992, **114**, 1518–1520; (*b*) B. V. Mork and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2003, **42**, 357–360; (*c*) X. Wang and L. Andrews, *J. Am. Chem. Soc.*, 2008, **130**, 6766–6773; (*d*) A. C. Filippou, O. Chernov, K. W. Stumpf and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2010, **49**, 3296–3300; (*e*) P. G. Hayes, Z. Xu, C. Beddie, J. M. Keith, M. B. Hall and T. D. Tilley, *J. Am. Chem. Soc.*, 2013, **135**, 11780–11783; (*f*) A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2014, **53**, 565–570.

8 (*a*) D. A. Straus, C. Zhang, G. E. Quimbita, S. D. Grumbine, R. H. Heyn, T. D. Tilley, A. L. Rheingold and S. J. Geib, *J. Am. Chem. Soc.*, 1990, **112**, 2673–2681; (*b*) H. Wada, H. Tobita and H. Ogino, *Organometallics*, 1997, **16**, 2200–2203; (*c*) S. H. A. Petri, D. Eikenberg, B. Neumann, H.-G. Stammler and P. Jutzi, *Organometallics*, 1999, **18**, 2615–2618; (*d*) C. Zhang, S. D. Grumbine and T. D. Tilley, *Polyhedron*, 1991, **10**, 1173–1176; (*e*) K. Ueno, H. Tobita, S. Seki and H. Ogino, *Chem. Lett.*, 1993, 1723–1726; (*f*) M. Okazaki, H. Tobita and H. Ogino, *Chem. Lett.*, 1996, 477–478; (*g*) M. Okazaki, H. Tobita, Y. Kawano, S. Inomata and H. Ogino, *J. Organomet. Chem.*, 1998, **553**, 1; (*h*) G. P. Mitchell and T. D. Tilley, *J. Am. Chem. Soc.*, 1997, **119**, 11236–11243; (*i*) S. K. Grumbine, G. P. Mitchell, D. A. Straus, T. D. Tilley and A. L. Rheingold, *Organometal-*

lics, 1998, **17**, 5607–5619; (*j*) M. Okazaki, H. Tobita and H. Ogino, *Dalton Trans.*, 2003, 493–506.

9 (*a*) J. Zhu, C. Dahlstrand, J. R. Smith, S. Villaume and H. Ottosson, *Symmetry*, 2010, **2**, 1653–1682; (*b*) J. Zhu, S. Bhandary, B. Sanyal and H. Ottosson, *J. Phys. Chem. C*, 2011, **115**, 10264–10271; (*c*) Q. Zhao, J. Zhu, Z. Huang, X. Cao and H. Xia, *Chem. - Eur. J.*, 2012, **18**, 11597–11603; (*d*) Y. F. Yang, G. J. Cheng, J. Zhu, X. Zhang, S. Inoue and Y. D. Wu, *Chem. - Eur. J.*, 2012, **18**, 7516–7524; (*e*) J. Zhu, K. An and P. v. R. Schleyer, *Org. Lett.*, 2013, **15**, 2442–2445; (*f*) J. Fan, K. An, X. Wang and J. Zhu, *Organometallics*, 2013, **32**, 6271–6276; (*g*) J. Zhu, H. A. Fogarty, H. Möllerstedt, M. Brink and H. Ottosson, *Chem. - Eur. J.*, 2013, **19**, 10698–10707; (*h*) 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; (*i*) C. Huang, Y. Hao, Y. Zhao and J. Zhu, *Organometallics*, 2014, **33**, 817–822.

10 G. P. Elliott, W. R. Roper and J. M. Waters, *J. Chem. Soc., Chem. Commun.*, 1982, 811–813.

11 (*a*) H. Fischer, *Carbyne Complexes*, Wiley-VCH, Weinheim, 1988; (*b*) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, 5th edn, 2005.

12 (*a*) P. B. Glaser, P. W. Wanandi and T. D. Tilley, *Organometallics*, 2004, **23**, 693–704; (*b*) P. G. Hayes, C. Beddie, M. B. Hall, R. Waterman and T. D. Tilley, *J. Am. Chem. Soc.*, 2006, **128**, 428–429.

13 S. E. Wheeler, K. N. Houk, P. v. R. Schleyer and W. D. Allen, *J. Am. Chem. Soc.*, 2009, **131**, 2547–2560.

14 A. Sekiguchi, R. Kinjo and M. Ichinohe, *Science*, 2004, **305**, 1755–1757.

15 (*a*) P. v. R. Schleyer and F. Pühlhofer, *Org. Lett.*, 2002, **4**, 2873–2876; (*b*) C. S. Wannere, D. Moran, N. L. Allinger, B. A. Hess Jr., L. J. Schaad and P. v. R. Schleyer, *Org. Lett.*, 2003, **5**, 2983–2986.

16 (*a*) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318; (*b*) H. Jiao, P. v. R. Schleyer, Y. Mo, M. A. McAllister and T. T. Tidwell, *J. Am. Chem. Soc.*, 1997, **119**, 7075–7083; (*c*) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888; (*d*) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Org. Lett.*, 2006, **8**, 863–866.

17 (*a*) E. D. Glendening, *et al. NBO 5.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2001; (*b*) The LanL2DZ basis set was employed to describe Os, Si, P, Cl whereas the standard 6-311++G(d,p) basis set was used for all other atoms for NICS calculations.

18 (*a*) M. A. Iron, A. C. B. Lucassen, H. Cohen, M. E. van der Boom and J. M. L. Martin, *J. Am. Chem. Soc.*, 2004, **126**, 11699–11710; (*b*) M. A. Iron, J. M. L. Martin and M. E. Van der Boom, *J. Am. Chem. Soc.*, 2003, **125**, 13020–13021; (*c*) C. Shi, T. Guo, K. Poon, Z. Lin and G. Jia, *Dalton Trans.*, 2011, **40**, 11315–11320.

19 S. Y. Yang, X. Y. Li and Y. Z. Huang, *J. Organomet. Chem.*, 2002, **658**, 9–14.

20 J. Zhu, G. Jia and Z. Lin, *Organometallics*, 2007, **26**, 1986–1995.

21 (*a*) H. Nakatsuji, J. Ushio and T. Yonezawa, *J. Organomet. Chem.*, 1983, **258**, C1–C4; (*b*) T. R. Cundari and M. S. Gordon, *J. Phys. Chem.*, 1992, **96**, 631–636; (*c*) A. Marquez and J. F. Sanz, *J. Am. Chem. Soc.*, 1992, **114**, 2903–2909; (*d*) K. Ueno, H. Tobita and H. Ogino, *J. Organomet. Chem.*, 1992, **430**, 93–104; (*e*) H. Jacobsen and T. Ziegler, *Organometallics*, 1995, **14**, 224–230; (*f*) H. Ogino, *Chem. Rec.*, 2002, **2**, 291–306.

22 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (*b*) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206; (*c*) C. Lee, W. Yang and G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785–789; (*d*) P. J. Stephens, F. J. Devlin and C. F. Chabalowski, *J. Phys. Chem.*, 1994, **98**, 11623–11627.

23 (*a*) A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111–114; (*b*) A. Höllwarth, H. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 237–240; (*c*) C. E. Check, T. O. Faust, J. M. Bailey and B. J. Wright, *J. Phys. Chem. A*, 2001, **105**, 8111–8116.

24 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654.

25 (*a*) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241; (*b*) Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157–167.

26 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.

27 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford, CT, 2009.

28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, V. G. Cheeseman, J. A. Montgomery, T. Vreven Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision E.01*, Gaussian, Inc., Wallingford, CT, 2004.

29 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.

30 (*a*) A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.*, 1990, **92**, 5397–9403; (*b*) A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuss and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 409–412; (*c*) B. Silvi and A. Savin, *Nature*, 1994, **371**, 683–686; (*d*) A. Savin, B. Silvi and F. Colonna, *Can. J. Chem.*, 1996, **74**, 1088–1096; (*e*) M. Kohout and A. Savin, *Int. J. Quantum Chem.*, 1996, **60**, 875–882; (*f*) A. Savin, R. Nesper, S. Wengert and T. Fässler, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1808–1832; (*g*) D. Marx and A. Savin, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2077–2080; (*h*) S. Noury, F. Colonna, A. Savin and B. Silvi, *J. Mol. Struct.*, 1998, **450**, 59–68.