RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *RSC Adv.*, 2020, **10**, 25275

Globally stabilized bent carbon–carbon triple bond by hydrogen-free inorganic–metallic scaffolding Al_4F_6†

Ying-ying Xue,[a] Ying Zhang,[a] Zhong-hua Cui *[b] and Yi-hong Ding *[ac]

Received 11th March 2020
Accepted 16th June 2020

DOI: 10.1039/d0ra02280b

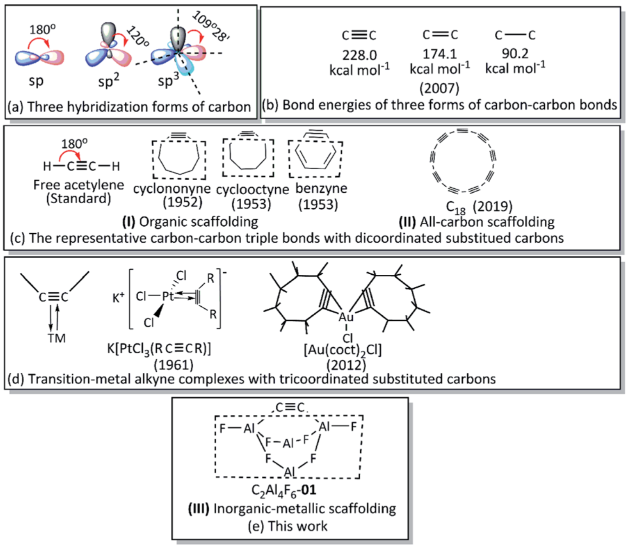
rsc.li/rsc-advances

For over 100 years, known bent C≡C compounds have been limited to those with organic (I) and all-carbon (II) scaffoldings. Here, we computationally report a novel type (III) of bent C≡C compound, *i.e.*, $C_2Al_4F_6$-**01**, which is the energetically global minimum isomer and bears an inorganic–metallic scaffolding and unexpected click reactivity.

1. Introduction

Carbon, the element with $2s^22p^2$ electron configuration, has three different hybridization forms of the valence atomic orbitals, *i.e.*, sp, sp^2 and sp^3 hybrid orbitals, with significantly more acute bond angles and decreased homo-atomic bond strength (see Schemes 1a and b).[1] Understandably, bending a C≡C bond is in most cases geometrically and electronically unfavourable. In fact, in acyclic or less strained cyclic compounds, the ∠CCR angle of C≡C is strictly 180° (*e.g.*, acetylene in Scheme 1c) or very close to 180° (*e.g.*, acyclic alkynes[1b,2] and other substituted compounds[3]). A significantly bent C≡C without additional coordination is only possible when it is embedded in highly strained or cyclic scaffoldings. As for most exotic species,[4] the conceptual and synthetic challenges of developing compounds with a significantly bent C≡C bond have been long attempted.[5] The first postulation of a bent C≡C constrained in an aromatic framework as an reactive intermediate was published more than one century ago (in 1902).[6] Since then, related species with bent C≡C bonds in organic scaffolding (see type **I** in Scheme 1c) have witnessed fruitful achievements, including applications in the pharmaceutical chemistry, materials chemistry, natural products synthesis, and organometallic chemistry.[5c,7] Cycloalkynes or angle-strained alkynes have received great attention due to their closeness to alkenes (obtained by simply losing two ligands).[5b–5h,7] Besides, mono-cyclic all-carbon molecules, *i.e.*, cyclocarbon[*n*], present the second class (see type **II** in Scheme 1c), each of which possess alternating C≡C and C–C bonds.[5a,8] After lengthy pursuit, the first ring-shaped molecule of pure carbon, *i.e.*, cyclocarbon (C_{18}), was recently synthesized, representing a breakthrough and possibly advancing potential molecular-scale electronic applications (*e.g.*, semiconductors).[5a,9]

One should be aware that when an alkyne perpendicularly interacts with a transition metal (TM) complex, so-called "transition-metal alkyne complexes" form (see Scheme 1d).[10] However, rather than the strain in type **I** and **II**, the synergistic bonding interactions between C≡C and TM in these complexes bend the C≡C, and the coordination number of the carbon atoms is increased to three rather than two in **I** and **II**. Thus,



Scheme 1 Hybridization forms and homo-nuclear bond energies of carbon, and representative compounds with carbon–carbon triple bonds.

---

[a] Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, P. R. China. E-mail: yhdd@jlu.edu.cn

[b] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130023, P. R. China. E-mail: zcui@jlu.edu.cn

[c] Key Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China

† Electronic supplementary information (ESI) available: Method details, Cartesian coordinates and total energies computed of key structures of $C_2Al_4F_6$ at the CBS-QB3 level, and some important information of the reactivity. See DOI: 10.1039/d0ra02280b

such compounds are not the topic of the present work. Moreover, one should note that in numerous cases, the TM-C≡C interactions may be so strong that the hybridization state of the ethynyl carbon atoms can change from sp to sp^2 upon coordination, greatly reducing or even diminishing the C≡C feature.[10a,10d,10g]

Can a significantly bent C≡C bond be stabilized by a non-carbon-based scaffolding while maintaining the dicoordinate carbons? We speculated that fluorinated metal dicarbides might possess the desired bent C≡C bond if metal fluorides can form stable and closed structures. During our study on F-persubstituted dicarbalanes ($C_2Al_4F_6$), by means of an extensive structural search and high-level energy calculations, we fortunately found a novel type (**III**) in which a bent C≡C bond can be globally stabilized by the novel scaffolding Al_4F_6 that is hydrogen-free and non-carbon-based. The global structure of $C_2Al_4F_6$-**01** has an interesting "flower-basket" shape (with an Al–F alternative 8-member ring tray and a C–C handle). The nature and reactivity of C≡C within the global $C_2Al_4F_6$-**01** was further studied *via* numerous analytic methods.

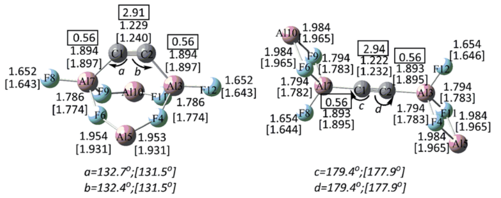
2. Theoretical methods

Due to the good balance between reliability and computational cost, the density function theory (DFT) method is now indispensable for studying molecules and materials, though debates still exist.[11] First, to obtain the global structure, we reasonably assumed that the fluorine atoms act as ligands around the C_2Al_4-core. We then applied our locally developed "skeleton-ligand cluster-growth" method[12] at the level of B3LYP[13]/6-31G(d), which has been shown to be quite cost-effective for initial large-scale isomeric searches. Further, those with energies lower than 20 kcal mol^{-1} were refined at the composite CBS-QB3 (ref. 14) level, which reliably gives accurate thermochemical properties in numerous fields. Second, similar to most DFT methods, the presently applied B3LYP is of single-reference nature and is constructed empirically *via* parameterization. The geometries, energetics and *T*1 diagnostics[15] of the former two lowest-energy isomers were computed using wave function-based methods, *i.e.*, CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVTZ. The single-point CBS-QB3 energies were recomputed at CCSD/cc-pVTZ and CCSD/6-311G(2d,d,p) geometries. Their geometries were also optimized at the M062X/6-311G(2d,d,p) level.

Natural bond orbital (NBO)[16] analysis and adaptive natural density partitioning (AdNDP) analysis[17] were conducted to understand their electronic structures at the B3LYP/6-311G(2d,d,p) level. The AdNDP analysis was analyzed by the Multiwfn program.[17b] All these calculations were performed using the commercial Gaussian 16 (ref. 18) and Gaussian 09 (ref. 19) packages.

3. Results and discussion

An amazingly large number, *i.e.*, 28600, of $C_2Al_4F_6$ isomers were obtained as local energy minima at the B3LYP/6-31G(d) level. For brevity and easy discussion, we only show the first two low-energy isomers with the respective bent and linear forms of C≡C, *i.e.*, **01** and **02**, at the CBS-QB3 level (see Fig. 1). Notably, the zero-point energy (ZPE)-corrected CBS-QB3 energy of **01** is lower than that of **02** by 2.4 kcal mol^{-1}. However, the relative Gibbs free energy between **01** and **02** is very close, with the latter lower by 0.6 kcal mol^{-1}. This suggests the profound influence of the Gibbs free energies on the stability of **01** and **02**. Thus, we performed additional calculations at the CBS-QB3 level using the costly CCSD/cc-pVTZ and CCSD/6-311G(2d,d,p)-optimized geometries. At the two CBS-QB3//CCSD levels, the Gibbs free energy of **01** is slightly more stable than **02** by 3.5 and 5.4 kcal mol^{-1}, respectively. Thus, **01** can be viewed as the global minimum.



	01	02
ΔE (CBS-QB3 level):	0.0	2.4
ΔG (CBS-QB3 level):	(0.0)	(-0.6)
ΔG (CBS-QB3//CCSD/cc-pVTZ level):	<0.0>	<3.5>
ΔG (CBS-QB3//CCSD/6-311G(2d,d,p) level):	{0.0}	{5.4}

Fig. 1 The key geometrical parameters (distances in Å and angles in (°)) at the CBS-QB3 and CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVTZ (in []) levels. The Wiberg bond indexes are shown in rectangular boxes. The relative CBS-QB3 energies (in kcal mol^{-1}) with zero-point correction (ΔE) and the relative Gibbs free energies (ΔG) of the former two isomers of $C_2Al_4F_6$ at different levels are shown.

Besides, since the *T*1 values of **01** and **02**, *i.e.*, 0.0137 and 0.0136, respectively, are considerably smaller than the recommended threshold value 0.02,[15] there should be negligible multi-reference characters for both structures. Note that the main bond distances and angles of $C_2Al_4F_6$-**01** and **02** are consistent among the CBS-QB3, CCSD and M062X levels (see Table S1†). Thus, for consistency, the following discussions are based on the CBS-QB3 values unless otherwise specified.

Bonding features of C≡C bond and C–Al bonds in $C_2Al_4F_6$-01 and 02

By comparing the corresponding typical triple and double carbon–carbon bond distances, *i.e.*, 1.198 Å in HC≡CH and 1.327 Å in $H_2C{=}CH_2$ at the B3LYP/6-311G(2d,d,p) level (see Fig. S7†), both **01** and **02** with very short CC distances (1.229 and 1.222 Å, respectively) can be viewed as containing a C≡C moiety, which is further supported by their large WBI values of 2.91 and 2.94, respectively. The C≡C bond of **01** is heavily bent, with two acute ∠CCAl angles of 132.7° and 132.4°. By contrast, **02** has an almost linear C≡C bond with a ∠CCAl angle of 179.4°.

The Al–F bonds in both **01**/**02** can be categorized into three classes, *i.e.*, 1.652/1.654, 1.786/1.794, and 1.954/1.984 Å, respectively, with increasing bond distances. The first two are comparable to the corresponding terminal (1.638 Å) and bridge (1.821 Å) Al–F bonds of the model Al_2F_6 (see Fig. S7†). The third type with the longer Al–F distance can be viewed as the dative bonding, indicating the presence of two Al^+-ions in **01**/**02**. The low-valent Al^+-subunits[20] are effectively stabilized by the neighbouring F → Al donor–acceptor interactions rather than the electron-sharing one. The situation is quite similar to the reference molecule Al_2F_4,[21] which has a ground ionic structure $Al^+[AlF_4]^-$ with the two types of Al–F bonds, *i.e.*, 1.993 Å between Al^+ and F and 1.648/1.783 Å between Al^{3+} and F (see Fig. S7†). Compared to the typical C–Al single bond of the model molecule $Al(CH_3)_3$ (1.967 Å), the C–Al bonds of **01** and **02**, *i.e.*, 1.894, 1.894, 1.893 and 1.893 Å, can be viewed as covalent single bonding. The somewhat shortened (smaller by 3.7%) bond of C–Al could result from the additional interaction between the Al-center and the similar C≡C π bond in **01** and **02**.

Note that the isomer **02** has a rather small low frequency (2.2 cm^{-1}). Its local minimum was confirmed at the MP2/6-311G(2d,d,p) level (5.4 cm^{-1}) (see Fig. S10†). The small low frequency indicates that **02** is a very floppy structure due to the two Al^+-ions stabilized by dative bonding. In fact, in bonds associated with easy rotation or wagging, very small low frequencies are evident. For example, in a small H-terminated cluster of graphene with 6 benzene units and 6 CC units, the first two imaginary frequencies are as small as 7.1 cm^{-1} and 7.2 cm^{-1} at the B3LYP/6-311G(2d,d,p) level, which correspond to the up-and-down wagging of the benzene unit.

The main molecular orbitals of isomers **01** and **02** are shown in Fig. 2. Both possess one σ bond, HOMO-4 (**01**) and HOMO-4 (**02**), and two π bonds (HOMO-2 and HOMO-3 for **01** and HOMO-2 and HOMO-3 for **02**). Each has two σ C–Al bonds (HOMO-10 and HOMO-11 in **01** and HOM0-12 and HOMO-15 in **02**). The widely used and efficient method, namely adaptive natural density partitioning (AdNDP) analysis,[17] was adopted at the B3LYP/6-311G(2d,d,p) level. The one 2c–2e σ (two centers and two electrons) bond and two 2c–2e π bonds with high occupation numbers (close to 2.0) support the presence of a triple C≡C bond and the high occupation numbers (close to 2.0) of two 2c–2e C–Al bonds well support the presence of the two C–Al the single bonds in both **01** and **02**. The detailed orbital and AdNDP analysis can be found in Fig. S2 and S3.†

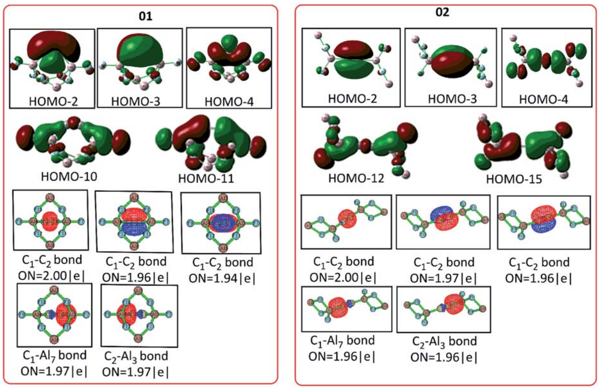
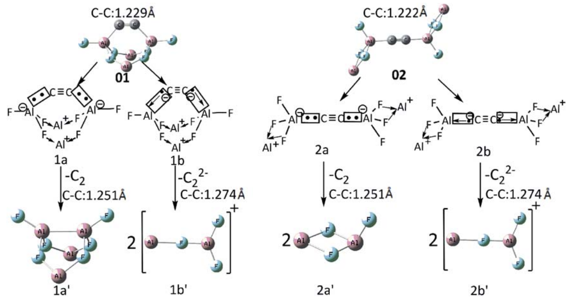


Fig. 2 The selected molecular orbitals of $C_2Al_4F_6$-**01** and **02** at the level of B3LYP/6-311G(2d,d,p). "ON" denotes the occupation number on the localized orbital.



Scheme 2 The path of eliminating C_2 and C_2^{2-} in $C_2Al_4F_6$-**01** and **02** at the level of B3LYP/6-311G(2d,d,p).

Based on the above structural and electronic analysis, we can deduce that the connection between C and Al should be of the "electron-sharing" type for both **01** and **02** (see **1a** and **2a** in Scheme 2) rather than the "electron dative" type (see **1b′** and **2b′** in Scheme 2). According to the "electron-sharing" mode, if C_2 is removed, the radical centers should be positioned at the neighbouring Al centers. This is well supported by the optimized $Al_2F_3^•$ and an Al–Al connected Al_4F_6 structure (see **1a′** and **2a′** in Scheme 2). However, the optimized fragments based on the "electron dative" mode, *i.e.*, $Al_2F_3^+$ and $Al_4F_6^{2+}$, differ rather dramatically from the structures of **01** and **02**.

Reactivity of C≡C in $C_2Al_4F_6$-01 and 02

Further, the presence of C≡C within the **01** and **02** isomers of $C_2Al_4F_6$ is consistent with the computational observation that the C≡C bond can undergo the addition of two H_2 molecules as well as [3 + 2] click reactions with HN_3. For known cycloalkynes, there is a clear linear correlation ($R^2 = 0.995$, see Fig. S11†) between the Gibbs free energy barriers and the bending angles of C≡C, *i.e.*, the higher bending degree of C≡C, the more reactive it becomes. The HN_3 click reactivity of **01** and **02** was a great surprise. Both have comparable barrier heights (20.3 and 21.2 kcal mol^{-1}, respectively) despite the significantly different bending angles of C≡C. The unexpected click reactivity of C≡C can be ascribed to the involvement of the neighbouring acid Al centers of **02** (see Fig. S4†). One of the Al^+ atoms of **02** could flip and attach to the nitrogen atom with the lone pair electrons of the HN_3 unit. Such additional interaction lowers the barrier of **02** with linear C≡C, approaching that of **01** with the bent C≡C bond. Compared with known cycloalkynes (see Fig. 3), the HN_3 click barrier (20.3 kcal mol^{-1}) of **01** lies between cycloheptyne (C_7H_{10}, 17.3 kcal mol^{-1}) and cyclooctyne (C_8H_{12}, 22.4 kcal mol^{-1}), indicating the feasible existence of **01** at least *via* spectroscopic detection.

Interconversion between $C_2Al_4F_6$-01 and 02

For the intrinsic stability, we attempted to identify the isomerization of the global isomer of $C_2Al_4F_6$-**01**. The lowest barrier is associated with an indirect conversion to $C_2Al_4F_6$-**02** by sequentially breaking the F → Al^+ dative bond *via* an intermediate $C_2Al_4F_6$-**18** (see Fig. 4). The barrier is as high as 14.8 kcal mol^{-1}. In addition, at the B3LYP/6-311G(2d,d,p) level,

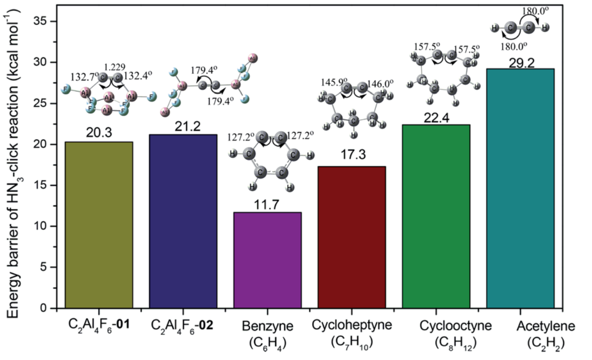


Fig. 3 Gibbs free energy barriers (in kcal mol^{-1}) of the HN_3 click reaction with $C_2Al_4F_6$-**01**, $C_2Al_4F_6$-**02**, benzyne, cycloheptyne, cyclooctyne and acetylene at the CBS-QB3 level.

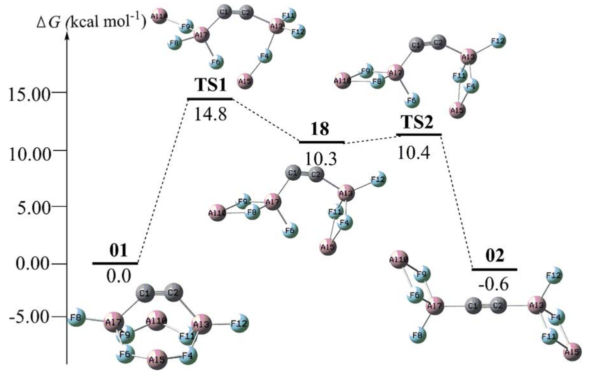


Fig. 4 The conversion pathways between $C_2Al_4F_6$-**01** and $C_2Al_4F_6$-**02** with the Gibbs free energy barriers at the CBS-QB3 level.

we obtained an optimized complex by adding two BH_3NH_3 to **01** (see Fig. S6†), which comprises four dative bonds, *i.e.*, two C → BH_3 and two NH_3 → C. This indicates that the bent C≡C bond in **01** does have the "hidden carbene" feature as was proposed very recently.[3a]

The unique stability of isomer **01** could be attributed to the balance of two opposite effects. On one hand, bending the C≡C bond leads to an energetic destabilization. On the other hand, the recombination of the two Al_2F_3 units causes energetic stabilization. Fig. 4 vividly shows this energetic change during the interconversion between **01** and **02**.

Implications

Two computational facts from the present work deserve the interest of the chemical community. First, our global isomeric search unexpectedly identified a bent C≡C bond (both C-atoms are in dicoordination) supported by a scaffolding that is neither of the two known carbon-based systems, *i.e.*, type-**I** and **II**. **01** presents the first example of a bent C≡C bond stabilized by an inorganic metal cluster composed of Al and F, despite the typical expectation that a polyatomic cluster such as $C_2Al_4F_6$ could sufficiently undergo complex structural rearrangement to avoid a global bent C≡C. Second, we observed an inverse click reactivity for C≡C between the inorganic metal-supported structures **01** (bent C≡C) and **02** (linear C≡C) due to the active involvement of the attached Al-atoms. We postulated that this structure could be versatile in such metal–inorganic C≡C compounds.

A large number of organometallic fluorides have been synthesized,[22] among which various C, Al, and F-based species are known.[23] Numerous general synthetic methods for generating angle-strained cycloalkynes have been reported.[5e] In our study, the lowest-energy $C_2Al_4F_6$-**01** with the bent C≡C bond has a high likelihood to be synthesized in future. Here, we tentatively supposed a possible synthetic method *via* the photochemical reactions of compounds $C_2Al_4F_6HCl$ or $C_2Al_4F_6CO$. We calculated the adsorption energy for removing HCl from $C_2Al_4F_6HCl$ at 273.15 K, which is 20.0 kcal mol^{-1} at the CBS-QB3 level. The process of removing CO from $C_2Al_4F_6CO$ was predicted to be exothermic by 9.3 kcal mol^{-1} at the CBS-QB3 level.

4. Conclusion

The unexpected finding of a bent C≡C bond stabilized globally within the chemical formula $C_2Al_4F_6$ contrasts sharply with the current knowledge of 6-vertex dicarbalanes, *i.e.*, $C_2Al_4R_6$ with R = H and CH_3 shows a distorted octahedral structure as the lowest energy isomer with the two carbons being well separated.[24] Besides providing of the great possibility to regulate the ground shape of dicarbalanes by substituent engineering, the strong tendency to form the triply bonded CC moiety indicates that a variety of low-lying bent C≡C with inorganic–metallic scaffoldings could be found in similar dicarbon metal fluorides (*i.e.*, $C_2M_xF_y$, M = heavier than group 13).

In summary, in this study, through our locally developed "skeleton-ligand cluster-growth" method, we report the first example of a main-group metal–inorganic compound isomer ($C_2Al_4F_6$-**01**) with a globally stabilized bent carbon–carbon triple bond. *Via* bonding analysis, we determined that $C_2Al_4F_6$-**01** exhibits a salt-like character with two $[-AlF_3]^-$ and two Al^+ units.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was funded by the National Key Research and Development Program of China (No. 2016YFB0701100) and the National Natural Science Foundation of China (No. 21473069, 21773082, 11922405). The authors are very grateful to the reviewers' invaluable comments and suggestions to improve our work.

Notes and references

1 (*a*) L. Pauling, *J. Am. Chem. Soc.*, 1931, **53**, 1367–1400; (*b*) M. B. Smith and J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, Wiley, New York, 6th

edn, 2007, pp. 3–136; (*c*) Y. R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC press, Boca Raton, 2007, pp. 147–154.

2 S. Patai, *The Chemistry of Carbon-Carbon Triple Bonds*, Wiley, New York, 1978, pp. 1–199.

3 (*a*) P. V. Bijina and C. H. Suresh, *ChemPhysChem*, 2018, **19**, 3266–3272; (*b*) D. C. Georgiou, L. L. Zhao, D. J. D. Wilson, G. Frenking and J. L. Dutton, *Chem.–Eur. J.*, 2017, **23**, 2926–2934; (*c*) D. C. Georgiou, B. D. Stringer, C. F. Hogan, P. J. Barnard, D. J. D. Wilson, N. Holzmann, G. Frenking and J. L. Dutton, *Chem.–Eur. J.*, 2015, **21**, 3377–3386.

4 (*a*) C. A. Dyker and G. Bertrand, *Nat. Chem.*, 2009, **1**, 265–266; (*b*) R. Hoffmann and H. Hopf, *Angew. Chem., Int. Ed.*, 2008, **47**, 4474–4481.

5 (*a*) K. Kaiser, L. M. Scriven, F. Schulz, P. Gawel, L. Gross and H. L. Anderson, *Science*, 2019, **365**, 1299–1301; (*b*) A. Das, C. Dash, M. Yousufuddin, M. A. Celik, G. Frenking and H. V. R. Dias, *Angew. Chem., Int. Ed.*, 2012, **51**, 3940–3943; (*c*) H. H. Wenk, M. Winkler and W. Sander, *Angew. Chem., Int. Ed.*, 2003, **42**, 502–528; (*d*) T. Kawase, Y. Seirai, H. R. Darabi, M. Oda, Y. Sarakai and K. Tashiro, *Angew. Chem., Int. Ed.*, 2003, **42**, 1621–1624; (*e*) A. Krebs and J. Wilke, *Angle strained cycloalkynes, Wittig Chemistry*, Springer, Berlin, Heidelberg, 1983, pp. 189–233; (*f*) J. D. Roberts Jr, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, 1953, **75**, 3290–3291; (*g*) A. T. Blomquist and L. H. Liu, *J. Am. Chem. Soc.*, 1953, **75**, 2153–2154; (*h*) A. T. Blomquist, L. H. Liu and J. C. Bohrer, *J. Am. Chem. Soc.*, 1952, **74**, 3643–3647.

6 R. Stoermer and B. Kahlert, *Ber. Dtsch. Chem. Ges.*, 1902, **35**, 1633–1640.

7 (*a*) K. Uchida, Y. Minami, S. Yoshida and T. Hosoya, *Org. Lett.*, 2019, **21**, 9019–9023; (*b*) T. Harris and I. V. Alabugin, *Mendeleev Commun.*, 2019, **29**, 237–248; (*c*) A. E. Goetz, T. K. Shah and N. K. Garg, *Chem. Commun.*, 2015, **51**, 34–45; (*d*) T. H. Poole, J. A. Reisz, W. Zhao, L. B. Poole, C. M. Furdui and S. B. King, *J. Am. Chem. Soc.*, 2014, **136**, 6167–6170; (*e*) A. Bhunia, S. R. Yetra and A. T. Biju, *Chem. Soc. Rev.*, 2012, **41**, 3140–3152; (*f*) P. M. Tadross and B. M. Stoltz, *Chem. Rev.*, 2012, **112**, 3550–3577; (*g*) E. M. Sletten and C. R. Bertozzi, *Angew. Chem., Int. Ed.*, 2009, **48**, 6974–6998; (*h*) H. Pellissier and M. Santelli, *Tetrahedron*, 2003, **59**, 701–730.

8 (*a*) C. Neiss, E. Trushin and A. Görling, *ChemPhysChem*, 2014, **15**, 2497–2502; (*b*) F. Diederich, *Nature*, 1994, **369**, 199–207; (*c*) V. Parasuk, J. Almölf and M. W. Feyereisen, *J. Am. Chem. Soc.*, 1991, **113**, 1049–1050; (*d*) F. Diederich, Y. Rubin, C. B. Knobler, R. L. Whettern, K. E. Schriver, K. N. Houk and Y. Li, *Science*, 1989, **245**, 1088–1090.

9 D. Castelvecchi, *Nature*, 2019, **572**, 426.

10 (*a*) K. D. J. Parker and M. D. Fryzuk, *Organometallics*, 2015, **34**, 2037–2047; (*b*) F. D. Rochon and C. Tessier, *Inorg. Chim. Acta*, 2007, **360**, 3533–3542; (*c*) M. A. Bennett and H. P. Schwemlein, *Angew. Chem., Int. Ed.*, 1989, **28**, 1296–1320; (*d*) R. S. Dickson and P. J. Fraser, Compounds Derived from Alkynes and Carbonyl Complexes of Cobalt, *Advances in Organometallic Chemistry*, Academic Press, 1974, vol. 12, pp. 323–377; (*e*) A. L. Beauchamp, F. D. Rochon and T. Theophanides, *Can. J. Chem.*, 1973, **51**, 126–131; (*f*) M. A. Bennett, G. B. Robertson, P. O. Whimp and T. Yoshida, *J. Am. Chem. Soc.*, 1971, **93**, 3797–3798; (*g*) G. R. Davies, W. Hewertson, R. H. B. Mais and P. G. Owston, *Chem. Commun.*, 1967, **9**, 423–424; (*h*) J. Chatt, R. G. Guy and L. A. Duncanson, *J. Chem. Soc.*, 1961, 827–834.

11 (*a*) S. Ghosh, P. Verma, C. J. Cramer, L. Gagliardi and D. G. Truhlar, *Chem. Rev.*, 2018, **118**, 7249–7292; (*b*) P. R. C. Kent and G. Kotliar, *Science*, 2018, **361**, 348–354; (*c*) S. Hammes-Schiffer, *Science*, 2017, **355**, 28–29; (*d*) M. G. Medvedev, I. S. Bushmarinov, J. W. Sun, J. P. Perdew and K. A. Lyssenko, *Science*, 2017, **355**, 49–52; (*e*) K. P. Kepp, *Science*, 2017, **356**, 496b; (*f*) M. G. Medvedev, I. S. Bushmarinov, J. W. Sun, J. P. Perdew and K. A. Lyssenko, *Science*, 2017, **356**, 496c.

12 (*a*) Y. H. Ding, *Skeleton-ligand Cluster-growth Isomeric Search Algorithm*, Jilin University, Changchun, China, 2014; (*b*) Y. Y. Xue and Y. H. Ding, *Chem. Commun.*, 2019, **55**, 6373–6376; (*c*) X. X. Bo, H. F. Zheng, J. F. Xin and Y. H. Ding, *Chem. Commun.*, 2019, **55**, 2597–2600; (*d*) Y. W. Sun, H. Y. Wang and Y. H. Ding, *RSC Adv.*, 2019, **9**, 40772–40780; (*e*) H. F. Zheng, S. Yu, T. D. Hu, J. Xu and Y. H. Ding, *Phys. Chem. Chem. Phys.*, 2018, **20**, 26266–26272; (*f*) J. Xu, X. Zhang, S. Yu, Y. H. Ding and K. H. Bowen, *J. Phys. Chem. Lett.*, 2017, **8**, 2263; (*g*) Y. Y. Xue, J. J. Sui, J. Xu and Y. H. Ding, *ACS Omega*, 2017, **2**, 5407–5414; (*h*) J. J. Sui, J. Xu and Y. H. Ding, *Dalton Trans.*, 2016, **45**, 56–60; (*i*) Z. H. Cui, Y. H. Ding, J. L. Cabellos, E. Osorio, R. Islas, A. Restrepo and G. Merino, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8769–8875; (*j*) X. Y. Zhang and Y. H. Ding, *RSC Adv.*, 2015, **5**, 27134–27139.

13 (*a*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789; (*b*) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627; (*c*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

14 (*a*) J. A. Montgomery, M. J. Frisch, J. W. Ochterski and G. A. Petersson, *J. Chem. Phys.*, 2000, **112**, 6532–6542; (*b*) J. A. Montgomery, M. J. Frisch, J. W. Ochterski and G. A. Petersson, *J. Chem. Phys.*, 1999, **110**, 2822–2827.

15 T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, 1989, **36**, 199–207.

16 E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, *NBO, version 3.1*, University of Wisconsin, Madison, WI, 1995.

17 (*a*) D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5207–5217; (*b*) T. Lu and F. W. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.

18 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini,

F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.

19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009.

20 (*a*) H. W. Roesky and S. S. Kumar, *Chem. Commun.*, 2005, **32**, 4027–4038; (*b*) M. N. S. Rao, H. W. Roesky and G. Anantharaman, *J. Organomet. Chem.*, 2002, **646**, 4–14.

21 T. Pankewitz, W. Klopper, P. Henke and H. Schnöckel, *Eur. J. Inorg. Chem.*, 2008, 4879–4890.

22 (*a*) S. Singh and H. W. Roesky, *J. Fluorine Chem.*, 2007, **128**, 369–377; (*b*) J. Pinkas and H. W. Roesky, *J. Fluorine Chem.*, 2003, **122**, 125–150; (*c*) B. Neumülle, *Coord. Chem. Rev.*, 1997, **158**, 69–101.

23 (*a*) H. Hatop, H. W. Roesky, T. Labahn, A. Fischer, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, 2000, **19**, 937–940; (*b*) C. Schnitter, K. Klimek, H. W. Roesky, T. Albers, H. G. Schmidt, C. Röpken and E. Parisini, *Organometallics*, 1998, **17**, 2249–2257; (*c*) Y. X. Chen, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1997, **119**, 2582–2583; (*d*) G. Natta, G. Allegra, G. Perego and A. Zambelli, *J. Am. Chem. Soc.*, 1961, **83**, 5033; (*e*) G. Gundersen, T. Haugen and A. Haaland, *J. Organomet. Chem.*, 1973, **54**, 77–86.

24 A. A. A. Attia, A. Lupan and R. B. King, *Inorg. Chem.*, 2015, **54**, 11377–11384.