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High-pressure stabilization of argon fluorides†‡

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On account of the rapid development of noble gas chemistry in the past half-century both xenon and krypton compounds can now be isolated in macroscopic quantities.[1] The same though does not hold true for the next lighter group 18 element, argon, which forms only isolated molecules stable solely in low temperature matrices or supersonic jet streams. Here we present theoretical investigations into a new high-pressure reaction pathway which enables synthesis of argon fluorides in bulk and at room temperature. Our hybrid DFT calculations (employing the HSE06 functional) indicate that above 60 GPa ArF_2-containing molecular crystals can be obtained by a reaction between argon and molecular fluorine.

Introduction

Over fifteen years after the successful synthesis of HArF[2] multiple other neutral Ar-containing molecules have been isolated and identified in both low-temperature matrices (*e.g.* ArBeS[3] or Ar complexes with CUO[4]) and in supersonic jet streams (*e.g.* ArAuCl[5]). Nevertheless Ar compounds in bulk quantities are yet to be synthesized. Although the substantial stability of the ArF^+ and ArH^+ cations led to a speculation that $ArX^+[MF_6]^-$ salts (X = F, H; M = Sb, Au) could constitute viable synthetic targets[6] to date such compounds have not been obtained.

The experimental pursuit for new connections of Ar has been aided by numerous theoretical predictions of possible new species, such as ArO_4,[7] $FBeAr^+$,[8] or $ArBeSO_4$,[9] to name just a few. Interestingly very little attention has been paid to the possible synthesis of ArF_2. We note that XeF_2 and KrF_2 *are* both known and are some of the most stable noble-gas compounds in general. To the best of our knowledge ArF_2 has not been synthesized up to now; we found only two theoretical investigations concerning this molecule dating back more than 25 years.[10]

It has been shown recently that high pressure (*i.e.* exceeding 1 GPa) can drastically alter chemical reactivity[11] thus enabling synthesis of new compounds otherwise not attainable at ambient conditions – in particular chemical connections of noble gases.[12] Indeed, multiple investigations concerning the high-pressure (HP) chemistry of xenon showed that at large compression this element reacts readily with silicon[13] and even water ice.[14] In addition, HP reactions of Xe with nickel and iron,[15] AuF_3,[16] as well as elemental oxygen[17] have been postulated on the basis of Density Functional Theory (DFT) calculations. However argon HP chemistry received less attention by theoreticians, although its melting curve,[18] and the high-pressure formation of molecular adducts with hydrogen were studied theoretically.[19]

Motivated by the possibility of stabilizing exotic noble gas containing species with the aid of high pressure (as exemplified by the predictions concerning the HP stabilization of HHeF[20]) we present theoretical investigations into a new high-pressure reaction pathway which enables synthesis of Ar connections with fluorine in bulk and at room temperature. With the use of an evolutionary algorithm we probe at selected pressures the potential energy surface (PES) of various Ar_mF_n stoichiometries, and show that above 60 GPa both argon difluoride (ArF_2) and a molecular complex of ArF_2 and F_2 ($ArF_2{\cdot}F_2{=}ArF_4$) can be synthesized from Ar and F_2.

Computational details

Accurate prediction of chemical reactions requires methods that correctly describe the thermodynamic stability of all the reactants. This requirement is particularly hard to

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† This work celebrates the 170th anniversary of the birth of Zygmunt Wróblewski, an eminent Polish physicist, who with Karol Olszewski was the first to liquefy oxygen and nitrogen.

‡ Electronic Supplementary Information (ESI) available: Computational details, calculated dissociation energies of F_2 and KrF_2, various Ar_mF_n structures and the pressure dependence of their enthalpy, phonon stability, ArF_2 synthesis from NF_3 and Ar, comparison of the PBE/HSE06/HSE06+D3 enthalpy-pressure curves, D3 corrections for Ar, F_2, ArF_2, ArF_4, optimized structures in VASP format. See DOI: 10.1039/x0xx00000x

fulfill for noble-gas compounds which often form hypervalent molecules. To ensure a correct description of the thermochemistry of the Ar/F_2 systems we tested several DFT methods based on the generalized-gradient approximation (GGA) and hybrid functionals by performing benchmark calculations for two molecules relevant to this study: F_2 and KrF_2 (a known analogue of the targeted ArF_2). We found that GGA methods fail to correctly describe the thermodynamic stability of these molecules while at the same time hybrid functionals yield results close to experiment‡. Therefore, we consistently used the hybrid HSE06 functional[21] in calculation of both the geometry and enthalpy of Ar_mF_n compounds, as well as the Ar and F_2 reaction substrates.

The candidate structure were identified with the use of the USPEX evolutionary algorithm[22] coupled with the PBE functional.§ All of the selected best candidate structures were subsequently re-optimized at the HSE06 level. The evolutionary search for stable structures of Ar_2F and ArF_n (n = 1 – 4) was performed at P = 100 and 200 GPa with 1, 2, and 4 formula units per cell. For more calculation details see ESI‡.

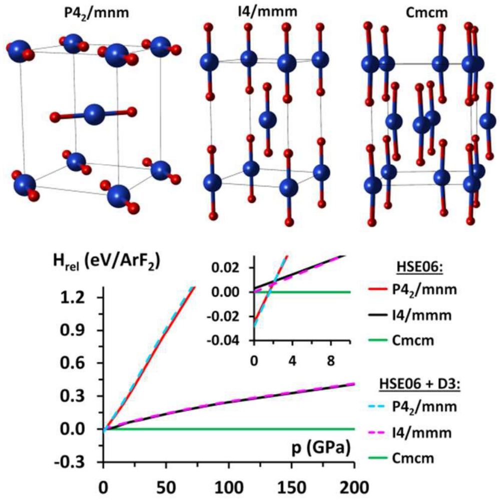

Fig. 2 Molecular crystals of ArF_2 (top, blue/red spheres depict Ar/F atoms) and the pressure dependence of their relative enthalpy (bottom, referenced to that of *Cmcm*) as calculated with HSE06 and HSE06 incorporating D3 dispersion corrections (see text).

Results and discussion

The pressure dependence of the calculated enthalpies of formation of numerous Ar_mF_n compounds (the so-called tie-line plot) is shown in Fig. 1. The results indicate that at approximately 60 GPa all of the considered argon fluorides (Ar_2F, and ArF_n, n = 1 – 4) become thermodynamically more stable than the respective mixtures of Ar and F_2. At even larger pressures the convex hull is dominated by a well-developed minimum at ⅔ F content (ArF_2 stoichiometry), which, as we will later show, corresponds to a molecular crystal composed of densely packed F-Ar-F units.

As noted, the enthalpy of formation of ArF_2 becomes negative above 58 GPa. In addition to ArF_2, a tetrafluoride, ArF_4, is also predicted to be stable (calculated pressure of formation equals to 54 GPa§§). The trifluoride, ArF_3, remains thermodynamically unstable in the whole pressure range studied (0 – 200 GPa); our calculation predict that ArF_3 would spontaneously decompose into ArF_2 and ArF_4. Similarly, both Ar_2F and ArF are predicted to decompose into a mixture of Ar and ArF_2. The dominance of ArF_2 over multiple other Ar_mF_n stoichiometries is evident upon inspection of their crystal structures‡. Indeed, all of the obtained Ar_mF_n structures contain isolated F-Ar-F units together with unbound Ar (in case of Ar_2F, ArF) or F_2 moieties (ArF_3 and ArF_4) . Thus, the chemically meaningful stoichiometries of these molecular complexes are as follow: $2Ar_2F = 3Ar{\cdot}ArF_2$; $2ArF = Ar{\cdot}ArF_2$; $2ArF_3 = 2ArF_2{\cdot}F_2$; $ArF_4 = ArF_2{\cdot}F_2$.

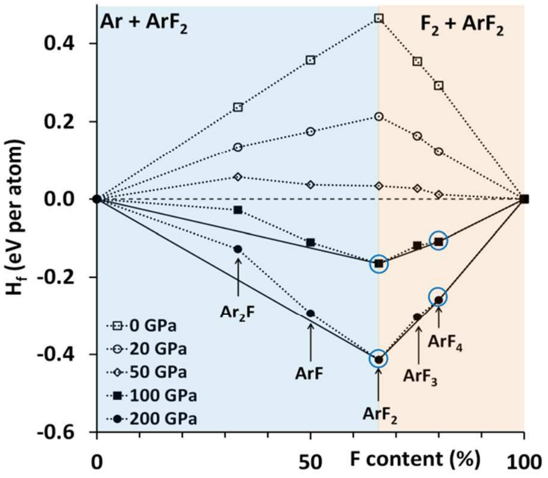

Fig. 1 Pressure dependence of the enthalpy of formation per atom of various Ar_mF_n phases. Compounds lying on the convex hull (marked with blue circles) are stable with respect to decomposition.

At ambient pressure (p ≈ 0 GPa) the lowest enthalpy structure of ArF_2 is a molecular crystal analogous to the high-temperature β phase of KrF_2 (*P4₂/mnm*);[23] at the same conditions, another polymorph – isostructural with the low temperature α form of KrF_2 (*I4/mmm*)[24] – is only 25 meV per formula unit (f.u.) higher in enthalpy. Both structures, shown in Fig. 2, contain linear and symmetric F-Ar-F molecules with bond lengths of 1.766 Å (*P4₂/mnm*) and 1.764 Å (*I4/mmm*).

As pressure increases both *P4₂/mnm* and *I4/mmm* destabilize with respect to a third polymorph of *Cmcm* symmetry. Already at 5 GPa this structure has the lowest enthalpy and it remains the most stable polymorph up to 200 GPa (Fig. 2). The *Cmcm* phase, similar to the theoretically predicted high-pressure form of XeF_2,[25] is also a molecular crystal. At the low-pressure limit (p = 5 GPa) it contains slightly bent F-Ar-F molecules (angle of 178.5°) albeit with fully symmetric Ar-F bonds (1.756 Å). Upon compression to 200 GPa the Ar-F bonds contract, by over 8 %, to 1.610 Å and remain symmetric. At the high-pressure limit, the ArF_2 molecules are more bent, although only slightly (173.9°). The molecular character of *Cmcm* is retained even at 200 GPa with the shortest intermolecular Ar···F contact (2.168 Å) being over 30 % longer than the intramolecular Ar-F bond. At 200 GPa the

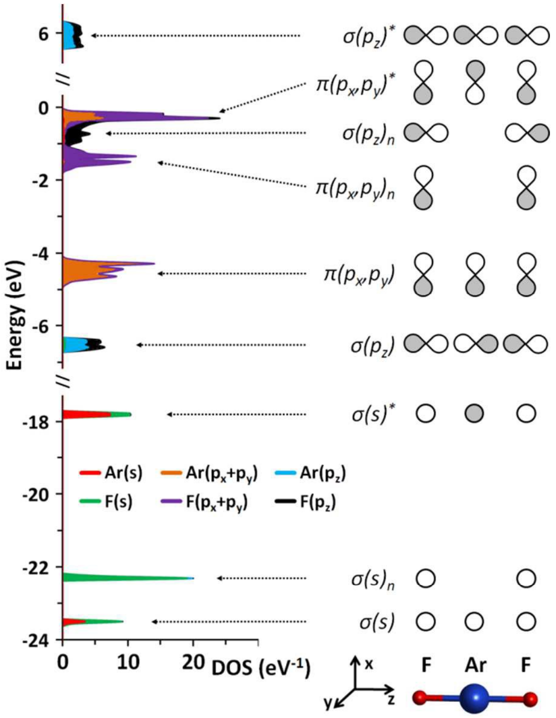

Fig. 3 Partial electronic density of states (DOS) per ArF_2 molecule of *$P4_2/mnm$* at 0 GPa together with a schematic depiction of the molecular orbitals of an isolated ArF_2 molecule. The p orbitals are labeled with respect to the internal coordinate system.

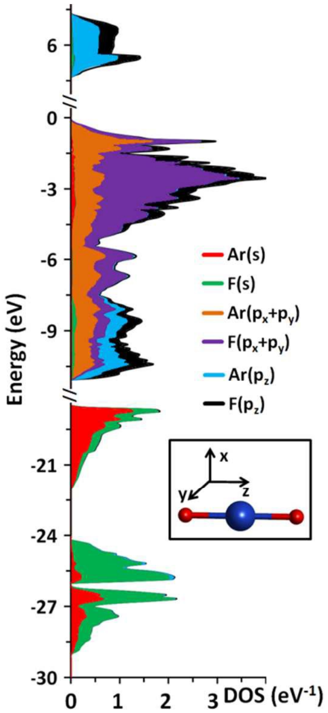

Fig. 4 Partial DOS per ArF_2 molecule of *Cmcm* at 100 GPa.

closest F···F contact (1.951 Å) is considerably longer than the F-F bond in pure F_2 at the same pressure (1.342 Å).

The molecular character of the ArF_2 phases is evident also upon inspection of the electronic density of states (DOS) (Fig. 3). At 0 GPa the *$P4_2/mnm$* structure is characterized by a wide band gap of 5.6 eV. Further analysis of the partial electronic DOS clearly shows that the character of electronic states of ArF_2 molecules can be understood within the framework of the Rundle-Pimentel electron-rich three-centre model[26]: one can identify states originating from bonding (σ, π), non-bonding (σ_n, π_n), and anti-bonding (σ^*, π^*) combinations of both *s* and *p* atomic orbitals. In agreement with the three-centre model the empty conduction band is derived from the σ^* combination of p_z orbitals.

We found that compression does not have any major impact on the band gap; it decreases only slightly, to 4.6 eV for *Cmcm* at 100 GPa (Fig. 4). Also the nature of the electronic states remains largely unchanged, with the separation between *s* and *p* states still clearly visible. We point that the partial DOS of both *$P4_2/mnm$* and *Cmcm* indicates no *d* orbital participation in the bonding, in analogy to what has been recently found for XeF_2.[27]

Turning to ArF_4 we recall that up to 200 GPa the ground state polymorph of this compound (of *C2/m* symmetry) is a molecular complex‡ of ArF_2 and F_2. In this structure the molecules occupy positions on a distorted NaCl lattice. Extrapolation of our results to higher pressures indicate that a structure containing genuine ArF_4 units becomes *the most stable* polymorph of ArF_4 only above 250 GPa. In other words, while oxidizing argon to the +2 oxidation state requires only 60GPa, a fourfold increase in pressure is require to stabilize this atom in the +4 oxidation state. While very high, such pressures are already obtainable.

The main driving force responsible for stabilization of both ArF_2 and ArF_4 with respect to Ar/F_2 mixtures is the volume reduction upon synthesis (7.5 and 5.1 % respectively, at 60 GPa). It's noteworthy to mention that pressures below 100 GPa are now easily accessible by standard experimental techniques utilizing diamond anvil cells (DACs). Moreover despite the very reactive and corrosive nature of fluorine this element has already been compressed in a DAC in the past.[28] The use of elemental F_2 as an oxidizing reactant is essential as our simulations indicate that replacing F_2 by less chemically aggressive nitrogen trifluoride (NF_3) - which has been recently proposed as a fluorinating agent in high-pressure reactions[29] - increases the pressure of ArF_2 synthesis well over 200 GPa‡.

The fact that the lowest enthalpy structures of ArF_2 and ArF_4 are molecular crystals indicates that inclusion of dispersion corrections[30,31] to the DFT hybrid functional may influence the thermodynamic stability of these phases. We have therefore calculated the so-called D3 correction[31] with Becke-Jonson damping[32] (using parameters given in ref. 33) for structures optimized with HSE06. For both ArF_2 and ArF_4 we found negligible differences in the pressure-enthalpy curves obtained with and without the dispersion corrections (see Fig. 2 and ESI‡). Although the values of these corrections reach up to –0.5 eV (ArF_2) and –0.6 eV (ArF_4) per f.u. at 200 GPa, the differences in these corrections between competing polymorphs are much smaller and do not exceed 0.05/0.04 eV per f.u. for ArF_2/ArF_4‡. Given the fact that the differences in enthalpy between various ArF_2 and ArF_4 phases are of an order of 1 eV (i.e. two orders of magnitude larger) the inclusion of the dispersion correction does not lead to any noticeable differences in the relative stability of ArF_2/ArF_4 phases nor in the pressure dependence of their enthalpy of formation‡.

Finally we would like to signal some important differences arising when the Ar/F system is calculated with the use of GGA (PBE functional) instead of the HSE06 hybrid functional‡. The energy of formation of an isolated ArF_2 molecule from Ar and F_2 calculated at the GGA/PBE level of theory is 116.3 kJ/mol, compared to a much larger value of 169.2 kJ/mol derived from the HSE06 calculations. Consequently GGA/PBE predicts a smaller synthesis pressure of *ca* 35 GPa for both ArF_2 and ArF_4. Underestimation of the pressure required for the stabilization of a particular compound might lead to errors in experiments, for example the synthesis might fail only because the pressure applied to the substrate mixture was not high enough. We also note that at the GGA/PBE level of theory Ar_mF_n phases that exhibit unrealistic bonding scenarios (such as -F-F- chains) are much more stabilized with respect to structures containing ArF_2 and F_2 molecules than for HSE06 calculations. These differences, steaming most likely from the lack of non-local exact exchange contributions in PBE, are yet another example of the deficiencies of GGA when calculating highly correlated systems subject to large compression.[34]

Conclusions

In conclusion we predict the possibility of the high-pressure stabilization of ArF_2-containing molecular crystals in macroscopic amounts and at room temperature. These compounds are the first examples of bulk systems containing covalently bonded argon. In case of ArF_2 we show that its bonding can be described with the electron-rich three-centre model, similarly to what is found for XeF_2 and KrF_2. Along with recent predictions of the HP stabilization of CsF_n ($n > 1$)[35] and HgF_4[36] our work is another example of the potential of high-pressure fluorine chemistry in stabilizing exotic hypervalent molecules. This rapidly growing field is paralleled by research on matrix isolation studies conducted in a highly oxidizing environment.[37]

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Notes and references

§ Due to the large computational cost of the calculations employing the HSE06 functional we were not able to employ it during the USPEX runs.

§§ Our phonon calculations (ESI‡) indicate that the lowest enthalpy structures of both ArF_2 and ArF_4 are dynamically stable in the thermodynamic stability fields of both compounds (*i.e.* above *ca* 60 GPa).

1 D. S. Brock, G. J. Schrobilgen, and B. Žemva, in *Comprehensive Inorganic Chemistry II*, Elsevier, 2013, vol. 1, pp. 755–822.
2 L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, and M. Räsänen, *Nature*, 2000, **406**, 874.
3 Q. Wang and X. Wang, *J. Phys. Chem. A*, 2013, **117**, 1508.
4 L. Andrews, B. Liang, J. Li, B. E. Bursten, *J. Am. Chem. Soc.*, 2003, **125**, 3126.
5 C. J. Evans, A. Lesarri, and M. C. L. Gerry, *J. Am. Chem. Soc.*, 2000, **122**, 6100.
6 G. Frenking, W. Koch, C. A. Deakyne, J. F. Liebman, and N. Bartlett, *J. Am. Chem. Soc.*, 1989, **111**, 31; K. O. Christe, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 1419; H. S. A. Elliott, J. F. Lehmann, H. P. A. Mercier, H. D. B. Jenkins, and G. J. Schrobilgen, *Inorg. Chem.*, 2010, **49**, 8504.
7 P. Pyykkö, *Phys. Scr.*, 1990, ***T33***, 52; R. Lindh, W. P. Kraemer, and M. Kämper, *J. Phys. Chem. A*, 1999, **103**, 8295.
8 M. Aschi and F. Grandinetti, *Angew. Chem. Int. Ed. Engl.*, 2000, **39**, 1690.
9 R. Saha, S. Pan, G. Merino, and P. K. Chattaraj, *J. Phys. Chem. A*, 2015, **119**, 6746.
10 R. Euler, B. Fricke, T. Morović, W.-D. Sepp, and A. Rosén, *Z. Phys. A: At. Nucl.*, 1980, **297**, 101; R. C. Catton and K. A. R. Mitchell, *Can. J. Chem.*, 1970, **48**, 2695.
11 W. Grochala, R. Hoffmann, J. Feng, and N. W. Ashcroft, *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 3620.
12 W. Grochala, *Chem. Soc. Rev.*, 2007, **36**, 1632.
13 C. Sanloup, B. C. Schmidt, E. M. Chamorro Perez, A. Jambon, E. Gregoryanz, and M. Mezouar, *Science*, 2005, **310**, 1174.
14 C. Sanloup, S. A. Bonev, M. Hochlaf, and H. E. Maynard-Casely, *Phys. Rev. Lett.*, 2013, **110**, 265501.
15 L. Zhu, H. Liu, C. J. Pickard, G. Zou, and Y. Ma, *Nat. Chem.*, 2014, **6**, 644.
16 D. Kurzydłowski and W. Grochala, *Z. Anorg. Allg. Chem.*, 2008, **634**, 1082.
17 Q. Zhu, D. Y. Jung, A. R. Oganov, C. W. Glass, C. Gatti, and A. O. Lyakhov, *Nat. Chem.*, 2013, **5**, 61; A. Hermann and P. Schwerdtfeger, *J. Phys. Chem. Lett.*, 2014, **5**, 4336.
18 J. Wiebke, E. Pahl, and P. Schwerdtfeger, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 13202.
19 C. Cazorla, D. Errandonea, and E. Sola, *Phys. Rev. B*, 2009, **80**, 064105; 1. C. Cazorla and D. Errandonea, *Phys. Rev. B*, 2010, **81**, 104108; Y. Yao and D. D. Klug, *Phys. Rev. B*, 2011, **83**, 020105.
20 Z. Bihary, G. M. Chaban, and R. B. Gerber, *J. Chem. Phys.*, 2002, **117**, 5105.
21 J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207; J. Heyd, G. E. Scuseria, *J. Chem. Phys.*, 2004, **121**, 1187; A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106.
22 A. R. Oganov, C. W. Glass, *J. Chem. Phys.*, 2006, **124**, 244704; C. W. Glass, A. R. Oganov, N. Hansen, *Comput. Phys. Commun.*, 2006, **175**, 713.
23 R. D. Burbank, W. E. Falconer, and W. A. Sunder, *Science*, 1972, **178**, 1285.
24 J. F. Lehmann, D. A. Dixon, and G. J. Schrobilgen, *Inorg. Chem.*, 2001, **40**, 3002.

25 D. Kurzydłowski, P. Zaleski-Ejgierd, W. Grochala, and R. Hoffmann, *Inorg. Chem.*, 2011, **50**, 3832.

26 R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, 1951, **73**, 4321; G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446.

27 B. Braïda and P. C. Hiberty, *Nat. Chem.*, 2013, **5**, 417.

28 R. D. Etters and D. Kirin, *J. Phys. Chem.*, 1986, **90**, 4670.

29 D. Kurzydłowski, H. B. Wang, I. A. Troyan, and M. I. Eremets, *J. Chem. Phys.*, 2014, **141**, 064706.

30 A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.*, 2009, **102**, 073005.

31 S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

32 S. Grimme, S. Ehrlich, and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.

33 J. Moellmann and S. Grimme, *J. Phys. Chem. C*, 2014, **118**, 7615.

34 E. Zurek and W. Grochala, *Phys. Chem. Chem. Phys.*, 2015, **17**, 291.

35 M. Miao, *Nat. Chem.*, 2013, **5**, 846; Q. Zhu, A. R. Oganov, and Q. Zeng, *Sci. Rep.*, 2015, **5**, 7875; A. Y. Rogachev, M. Miao, G. Merino, R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, 2015, 54, 8275.

36 J. Botana, X. Wang, C. Hou, D. Yan, H. Lin, Y. Ma, and M. Miao, *Angew. Chem. Int. Ed.*, 2015, **54**, 9280.

37 T. Vent-Schmidt, F. Brosi, J. Metzger, T. Schlöder, X. Wang, L. Andrews, C. Müller, H. Beckers, and S. Riedel, *Angew. Chem. Int. Ed. Engl.*, 2015, **54**, 8279; X. Wang, L. Andrews, S. Riedel, and M. Kaupp, *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 8371.