doi:10.2533/chimia.2012.418 Chimia 66 (2012) 418–424 © Schweizerische Chemische Gesellschaft

The Development of Organic Super Electron Donors

Shengze Zhou, Hardeep Farwaha, and John A. Murphy*

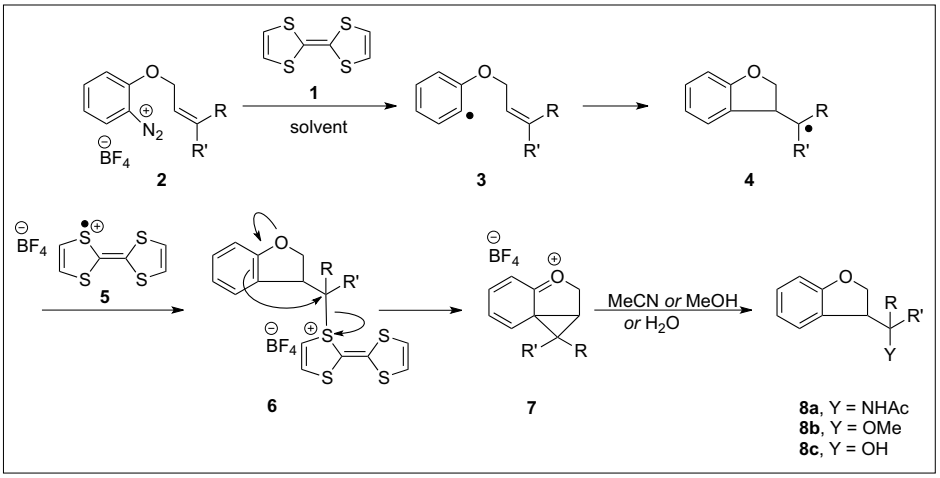
Abstract: In the past decade, a host of exceptionally strong organic electron donors has been designed and prepared; their redox potentials are more negative than any previous neutral organic donors and extend beyond $E_{1/2}$ = –1 V *vs*. the saturated calomel electrode (SCE). Their ability to reduce a wide range of organic functional groups has been demonstrated and this article provides an overview of the main advances in the area and the guiding principles for the design of these reagents.

Keywords: Carbene · Electron transfer · Radical anion · Radical cation · Reduction · Super-electron-donor

When particularly challenging reductions need to be undertaken, metals and metal complexes have been the reagents of choice. For example, Birch reduction of arenes[1] or alkynes is dependent upon highly reactive metals as the source of the solvated electrons that accomplish the reduction. Similarly, in enzymology, the nitrogenase enzymes that reduce dinitrogen to ammonia recruit molybdenum or vanadium or iron for their key functions.[2] But is such great reactivity intrinsically limited to metals, or could simple organic molecules be designed to compete? If the full range of reactivity could be established for organic electron transfer reagents, this would open up new reactions for use in chemical synthesis and new capabilities for organic materials, but it would also encourage reflection on wider issues: could simple organic systems evolve to cover critical biological redox processes in locations where key metals are sporadically distributed or absent?

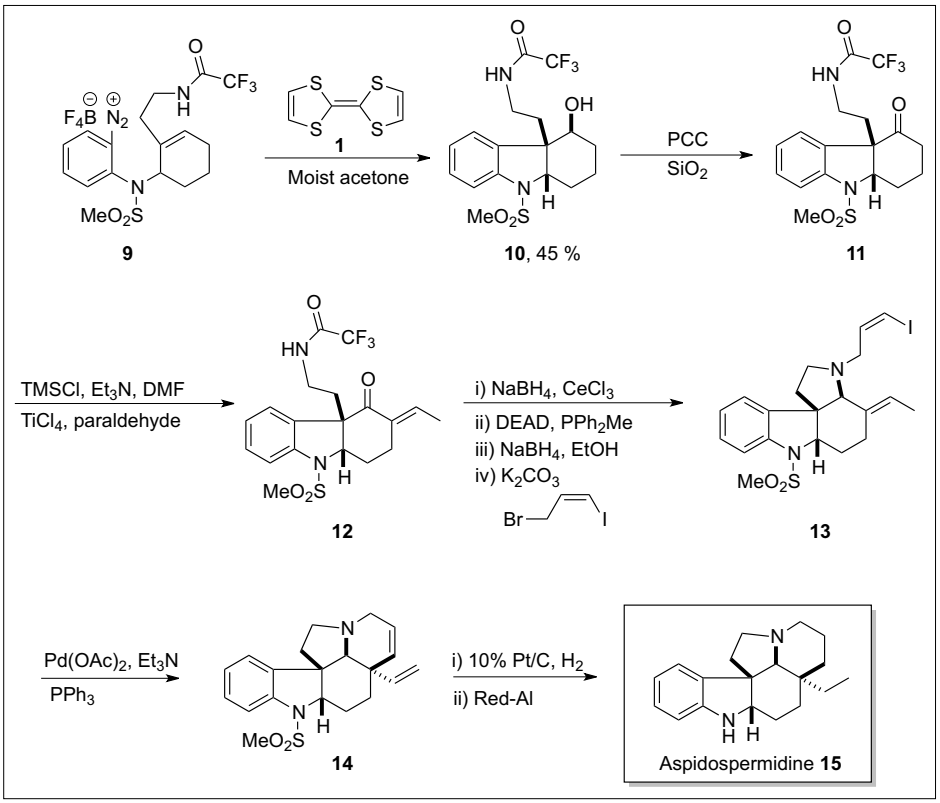
In 1970, Wudl announced[3] the synthesis of tetrathiafulvalene (TTF, **1**, Scheme 1); this followed work on analogous compounds[4] but his announcement turned a corner for organic electron donors. TTF is useful because it can be oxidized easily to its radical cation or, at more positive potential, to its dication; $E^1_{1/2}$ (MeCN) = +0.32 V; $E^2_{1/2}$ (MeCN) = +0.71 V *vs.* SCE.[5] In Web of Knowledge, TTF now has about 30,000 citations indicating the importance of TTF and its derivatives, particularly in the world of organic materials. However, aside from its ongoing uses for materials chemistry, this molecule also provided the introduction to reactive organic electron donors for our research group, as a prospective reagent in synthesis. Neiland and co-workers[6] had reported liberation of dinitrogen when diazonium salts were reacted with TTF. Our own study focused on the nature of the organic products. When diazonium salts, *e.g.* **2**, were treated with TTF (**1**) at room temperature, electron transfer occurred and dinitrogen was evolved (Scheme 1); the aryl radicals **3** cyclised and the resulting radicals **4** were then trapped by the radical-cation, $TTF^{+\bullet}$ (**5**).[7] The sulfonium salts **6** that formed in this step were generally very reactive; displacement of the TTF unit was effected in the presence of acetonitrile or methanol or water (water is always conveniently present when acetone is used as solvent) affording ultimately amides, ethers or alcohols respectively, with the amides arising from hydration of intermediate nitrilium salts on work-up. The substitutions on TTF salts were later shown to require neighbouring group assistance, as shown by the oxygen atom in **6** in Scheme 1.[8]

With that in mind, it might be expected that the displacement of the TTF leaving group would be easiest to achieve when the TTF-bearing carbon was primary (**6**, R = R' = H), but whereas secondary and tertiary carbons underwent easy displacement of the TTF leaving group, the primary carbon example was completely resistant to substitution, leading to the conclusion that the transition state for the displacement reaction was subtly more complex than expected. In any case, with the isolation of products **8** from all other substrates, TTF proved useful in providing a different type of termination for radical reactions, where initial radical steps had been followed by nucleophile/electrophile steps, for which the term 'radical-polar crossover' was adopted. This transformation was then deployed in a synthesis of (±)-aspidospermidine (**15**, Scheme 2).[9]



Scheme 1.

*Correspondence: Prof. Dr. J. A. Murphy
WestCHEM
Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street
Glasgow G1 1XL, UK
Tel.: +44 141 548 2389
E-mail: john.murphy@strath.ac.uk



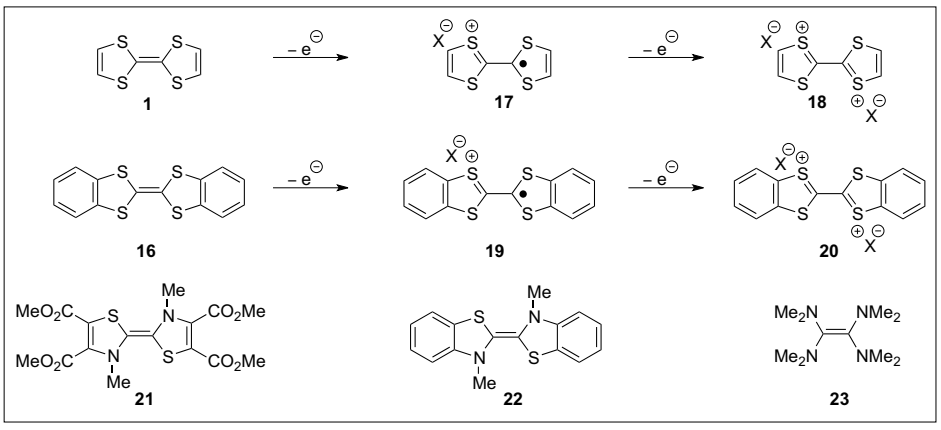
Scheme 2.

Whereas TTF was a useful electron donor for arenediazonium salts, we were also interested in reducing other organic substrates, notably iodoarenes. However, the oxidations of TTF ($E^1_{1/2}$ (MeCN) = +0.32 V; $E^2_{1/2}$ (MeCN) = +0.71 V *vs.* SCE[5] for sequential loss of two electrons, as mentioned above) occur at much more positive potentials than the reduction of iodoarenes (E^0 = –2.2 V)[10] so TTF is nowhere near powerful enough to effect that reaction. The design of suitable reagents to achieve this task became a focus of our attention.

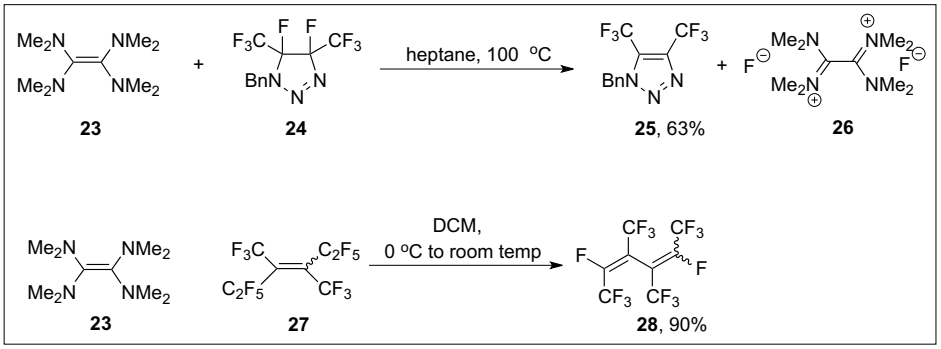
Progress relied on two principles. The first relates to aromaticity and derived from our previous efforts with TTF derivatives. Unlike TTF, dibenzoTTF (**16**) [$E^1_{1/2}$ (PhCN) = +0.60 V; $E^2_{1/2}$ (PhCN) = +0.98 V *vs.* Ag/AgCl][11] (equivalent to +0.56 V and + 0.94 V *vs.* SCE) was not able to reduce arenediazonium salts at ambient temperatures. Oxidation of compounds **1** and **16** produces the radical cations **17** and **19** respectively, and the radical cations can be represented (Scheme 3) in a way that shows a new aromatic five-membered ring, but the driving force associated with the generation of this new aromaticity differs in the two compounds. The newly aromatic five-membered ring in the radical cation **19** is part of a fused aromatic system and so, in simple terms, two atoms in the five-membered ring were already part of an aromatic ring in the starting donor **16**. In contrast, the conversion of **1** to **17** sees aromaticity created, and this implies a greater driving force for formation for **17** than for **19**. Hence aromaticity plays an important role in modulating the power of organic electron donors.

The second principle relates to the role of nitrogen atoms in assisting electron transfers. This is illustrated well in comparing TTF and compound **21**. The electron-withdrawing ester groups in **21** might lead one to suspect that TTF was the better electron donor. However, the redox potentials showed the tetraester [$E^1_{1/2}$ (MeCN) = –0.02 V; $E^2_{1/2}$ (MeCN) = +0.23 V *vs.* SCE)[12] was the stronger donor. So assistance provided by the two nitrogen atoms in **21** in replacing two sulfur atoms of TTF outweighs the opposition provided by the four esters. This effect could be ascribed to better π-overlap between N and C compared with that between S and C. Despite their greater reducing power than TTF, dithiadiazafulvalenes did not act as reducing agents for iodoarenes – we prepared related compounds including **22** and they did not achieve the reaction. [Polarographic studies showed closely related compounds have E^1 (MeCN) = –0.16 V and E^2 (MeCN) = – 0.021 V *vs.* Ag/AgCl,[13] (equating to –0.20 V and –0.06 V *vs.* SCE)].

Since two nitrogen atoms assisted electron transfer in diazadithiafulvalenes like **22**, then four nitrogen atoms should afford even stronger donors. Among the accessible tetraazaalkenes was the commercially available tetrakis(dimethylamino)ethene (TDAE, **23**) which had been discovered in Du Pont in 1950.[14] With oxidation potentials of –0.54 V and –0.37 V *vs.* SHE in MeCN (therefore –0.78 V and –0.61 *vs.* SCE) it is a relatively strong electron donor.[15,16] Early uses had seen this molecule defluorinate perfluorinated substrates, such as **24** and **27** (Scheme 4).[17]



Scheme 3.

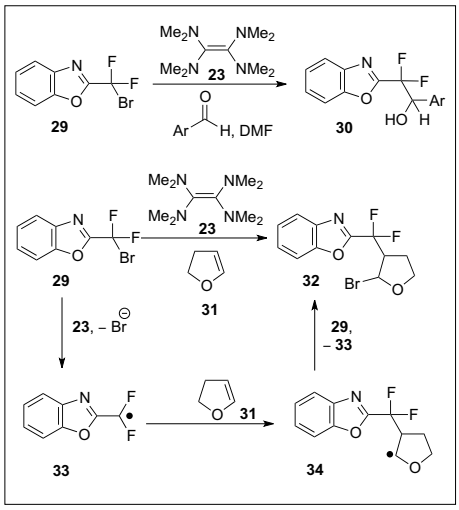


Scheme 4.

Médebielle and Dolbier and co-workers made extensive and elegant use of this reagent in converting CF_3I to the trifluoromethyl anion and in converting benzylic halides **29** to benzylic radicals or benzylic anions through transfer of one or two electrons respectively.[15,18] Scheme 5 shows an example of each, deriving from the same starting substrate, **29**. Nucleophilic addition of the derived benzylic anion to benzaldehydes afforded alcohols **30**, while trapping of the intermediate benzylic radical **33** by dihydrofuran **31** affords radical **34** that triggers atom transfer with bromide **29** to afford the isolated product **32**.

We also explored this reagent to see if it could reduce aryl halides, but had no success and we concluded that a more powerful reagent was needed. While it did not react with iodoarenes, it does react with diazonium salts.[19]

In mentioning compounds where oxidation is assisted by the presence of many appropriately placed nitrogen atoms, Himmel *et al.* prepared interesting compounds including **35** (Fig. 1).[20] A notable point about this molecule as a prospective electron donor is that it starts as an aromatic system, and therefore the stabilisation associated with generating aromaticity is not part of the driving force for its oxidation. Indeed, two-electron oxidation should convert it to a non-aromatic quinone-diiminium salt derivative **36**. Therefore, it may be no surprise that, in solution, its redox potential [$E^1_{1/2}$ (MeCN) = –0.25 V and $E^2_{1/2}$ (MeCN) = +0.50 V *vs.* SCE] showed that it was not as strong a reducing agent as TDAE (**23**) [$E_{1/2}$ (MeCN) = –0.78 V *vs.* SCE]. However, calculations suggested that in the gas-phase, it should be a leading electron donor.[20b] This may reflect the extensive delocalisation of charge in its oxidised states, with the outcome that its oxidised forms benefit less from solvation than some other donors.



Scheme 5.

Whereas compound **35** loses aromaticity on oxidation, three recent papers by Vaid and coworkers describe compounds that feature aromaticity in interesting ways. The most recent of these is the intriguing porphyrin-like structure **37**.[21] This compound has aromatic features in its starting neutral form, and so does its dication oxidised product, and so its oxidation should not be strongly driven by favourable changes in its aromaticity. This is reflected in its oxidation potentials, E^1 (THF) = –0.59 V and E^2 = –0.26 V *vs.* Fc/Fc$^+$ (= –0.14 V and + 0.19 V *vs.* SCE respectively). In contrast, the tetracyclic compound **38** can attain aromaticity in four rings by two-electron loss.[22] The authors discussed whether closed-shell structure **38** accurately describes the bonding in this compound or whether its ground state might be a diradical form of **38**. This question arose because the ^{1}H NMR spectrum of this compound featured broad resonances. Its structure was fully confirmed by X-ray crystallography. In cyclic voltammetry, it showed a single two-electron oxidation at E^1 (THF) = –1.48V *vs.* Fc/Fc$^+$ (equivalent to –1.03 V *vs.* SCE), making this compound the most reducing neutral organic ground-state compound at the time.

Vaid's group made another fascinating contribution to this field with the synthesis of **40**. This compound looks to have an enormous driving force for its oxidation, with up to seven rings capable of converting to aromatic rings.[23] Its redox properties are indeed interesting; starting with the oxidised form, the fully aromatic hexacation, **41**, cyclic voltammetry was marked by a 4-electron reduction [E^0_1 (THF) = –1.03 V *vs.* Fc/Fc$^+$ (= –0.58 V *vs.* SCE) and a 2-electron reduction [E^0_2 (THF) = –1.14 V *vs.* Fc/Fc$^+$ (= –0.69 V *vs.* SCE), and both processes appeared chemically reversible (*i.e.* no decomposition of reduced products). Surprisingly, the redox values show that **40** is not as reducing as TDAE (**23**). So despite the numbers of nitrogens capable of stabilising oxidised products, and despite the aromaticity of the oxidised products, other factors impede the oxidation and no full analysis of this has yet been announced.

Since TDAE is a relatively strong donor and a member of the tetraazafulvalene family, our quest continued by looking at other members of that family. As an electron donor, dibenzotetraazafulvalene **42** combines the benefits of four nitrogens with some aromatic driving force. This and related compounds had been prepared previously and their oxidation potentials determined.[13,24,25]

Compound **42** is simply formed by deprotonation of the disalt **44** which, in turn, is easily formed from *N*-methylbenzimidazole (**43**, Scheme 6). Cyclic voltammetry showed two one-electron reversible waves at $E^1_{1/2}$ (DMF) = –0.82 V in conversion to the radical cation **47**; $E^2_{1/2}$ (DMF) = –0.76 V *vs.* SCE for the conversion between **47** and the dication **48**.[13,24] However, studies of the reactivity of **42** as a reducing agent had been very limited and solely its reactions with O_2 had been explored.

In our hands, reaction of **42** with iodoarenes now showed success – it was the first neutral organic electron donor reagent that was able to reduce iodoarenes; appropriate substrates, **49**, afforded aryl radicals, as shown through efficient cyclisation onto alkenes in DMF as solvent (Scheme 7). Both iodoarenes and iodoalkanes were reduced in high yield and the product radicals trapped by cyclisation and then hydrogen abstraction. To test the origin of the abstracted hydrogen in **51**, d_7-DMF was used as solvent for the reduction of **49**, but this did not lead to labelled product, indicating that the abstracted hydrogen, very likely came from the donor **42** or its oxidised forms.[26]

The first redox value for donor **42** is

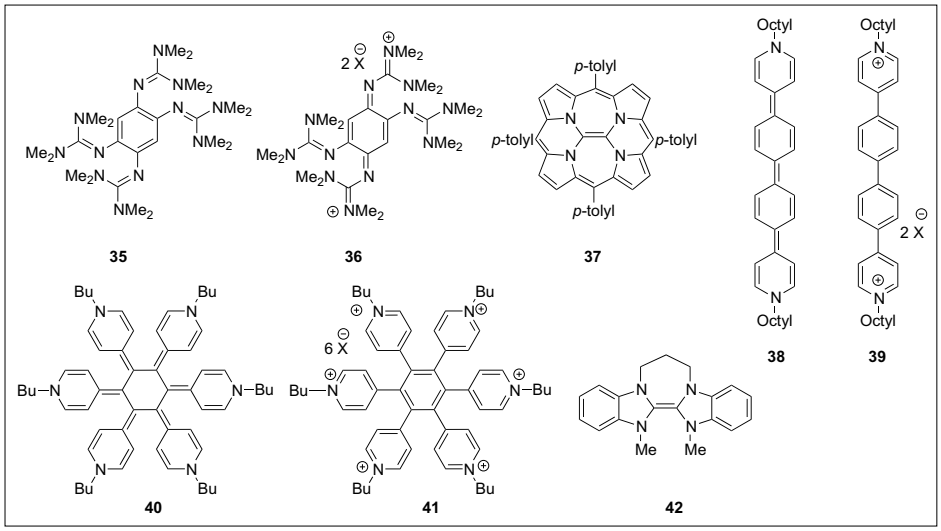
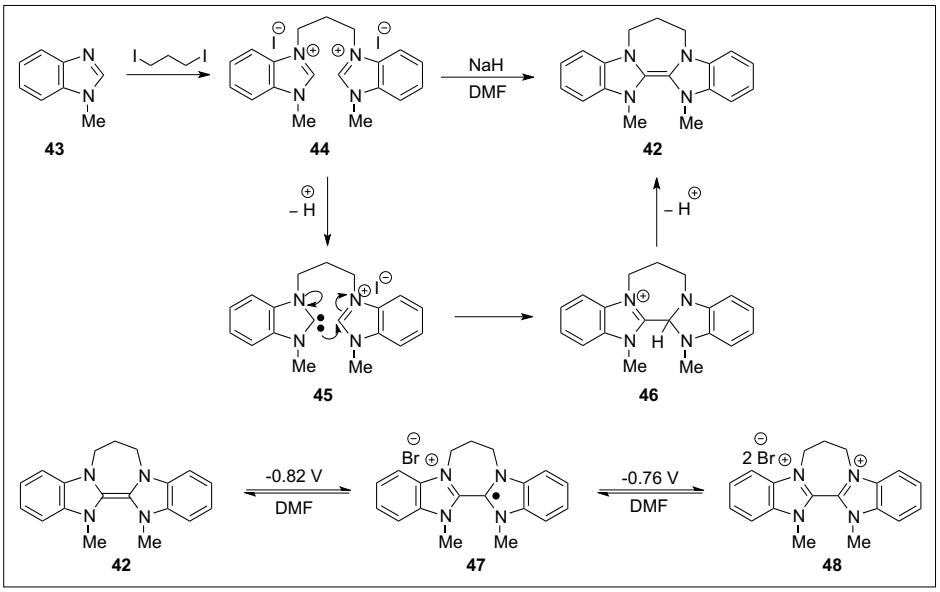
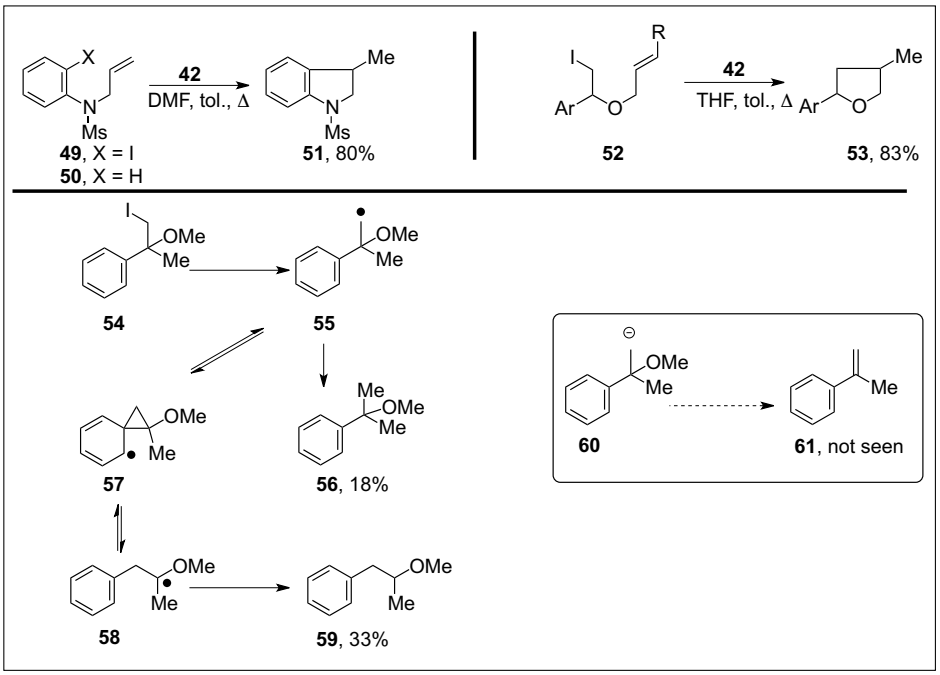


Fig. 1.



Scheme 6.

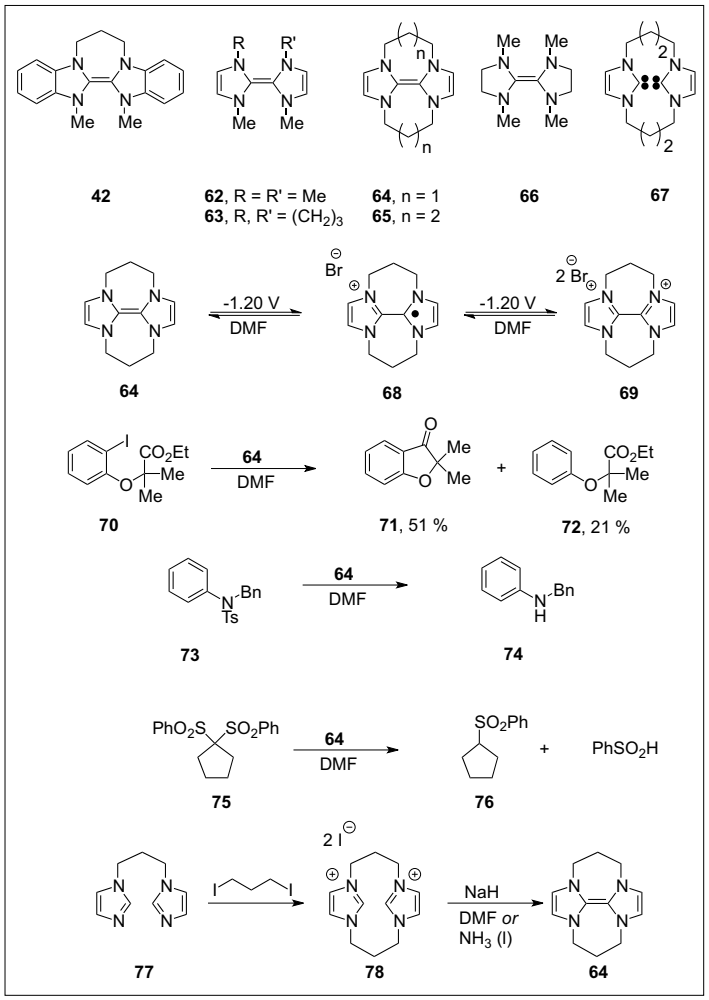
only slightly more negative than that for TDAE, and it falls well short of the reduction potential of an iodoarene; nevertheless, with the aid of some heat and by using a number of excess equivalents of the donor, reduction of substrates such as **49** was achieved in high yield.[27] The situation is even more curious than this; the reduction of an iodoarene could involve one-electron reduction to an aryl radical or two-electron reduction to an aryl anion, where an aryl radical was the intermediate. The standard reduction potential for an iodoarene is about –2.2 V, but this very negative potential must be associated with the first stage of the reactions as Andrieux and Pinson had shown that the standard potential for one-electron reduction of an aryl radical [to an aryl anion] was a very mild E^0 (MeCN) = +0.05 V.[28] Accordingly, in the reduction of iodobenzenes, the second reductive step is hugely easier to achieve than the first. Reagent **42** behaved strangely – it donated an electron for a reaction exceeding its reduction potential thereby forming an aryl radical, but had not reduced the aryl radical even though the reduction potential for this is easily within its thermodynamic scope. Accordingly, additional factors, which might be associated with the kinetics of the reduction, the nature of the counterions and solvent and the presence of donor-acceptor complexes, affect the reduction of the aryl radical to the intermediate aryl anion. In conversion of arenediazonium salts to aryl carboxylates, involving reaction of aryl anions with carbon dioxide, Otero *et al.* found empirically that a potential of about –1 V was required in practice to produce aryl anions from diazonium salts in solution.[29] This tallies with our findings below.



Scheme 7.

Besides reducing aryl iodides, this reagent also reduced alkyl iodides, *e.g.* **52**, to their radicals, as seen in this case in the high-yielding cyclisation to tetrahydrofuran **53**.[26] The intermediacy of alkyl radicals was also seen in a neophyl rearrangement of substrate **54**, with the two expected products, **56** and **59** being isolated from the reaction. Iodide **54** also acted as a probe for two-electron reduction, since that would be expected to afford α-methylstyrene **61**. Such a reduction would likely have occurred in concerted manner rather than forming the naked alkyl anion **60**. However, regardless of mechanism, **61** was not observed.

Plainly, donor **42** shows that the tetraazafulvalene reducing agents were worth pursuing. One way to make a stronger donor from the same family would be to use an *N*-alkylimidazole, rather than *N*-methylbenzimidazole **43**, as starting material. In fact studies in this area had already taken place. Thus, starting with the stable oxidised dication forms of such donors, cyclic voltammetry[24,25d] had shown that most compounds of this type did not afford reversible redox reactions – *i.e.* their reduction led to their decomposition. A detailed study was carried out by Taton and Chen,[30] who showed that the tetraazafulvalene **63** derived from *N*-methylimidazole could not be prepared. However, they did succeed in preparing the doubly trimethylene-bridged donor **64**. They also demonstrated the precarious existence of these compounds through the synthesis of the close analogue **65** which differs solely from **64** in the fact that the trimethylene bridges have been replaced by their tetramethylene counterparts.[30] This compound appeared to form at –78 °C but warming to room temperature was all that was needed to convert it into the bis-carbene **67** (Scheme 8). To underline the instability of these compounds, calculations suggested a 4kJ/mole bond energy value for the C=C bond in **62**, compared to a more normal value of 120 kJ/mole for the analogue **66**.[30,31] They showed that the beautiful yellow compound **64** however was stable in the absence of air and moisture, and so we determined its activity with a range of substrates. We wanted to know if this compound would form the aryl radical or if this could then be reduced to the corresponding aryl anion. Its reaction with iodoarenes gave different results than seen for donor **42**. With the substrate **49**, the cyclised product **51** was now a minor product, but the major product was the



Scheme 8.

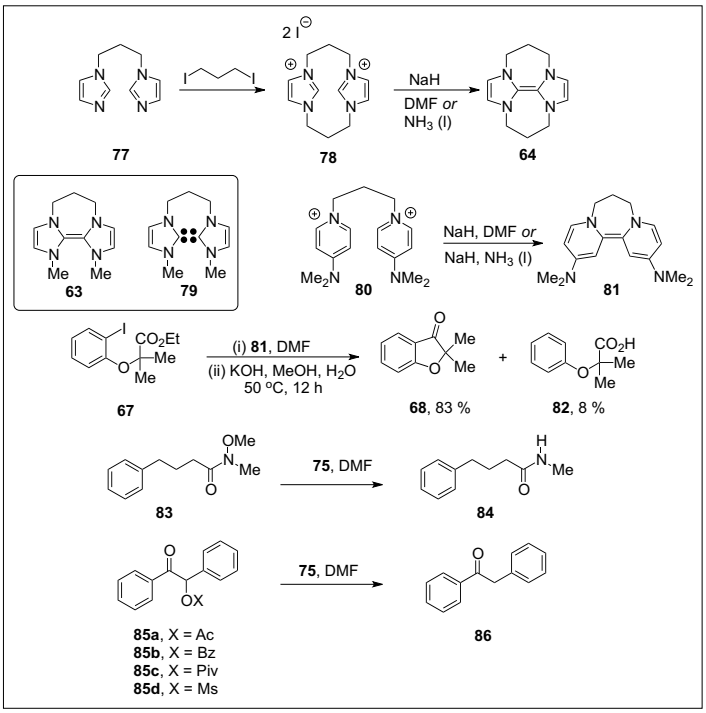
deiodinated uncyclised compound **50**. This suggested that a different intermediate had formed in this reaction than when **42** was the donor. Given the mild standard potential for reduction of an aryl radical[28] and the oxidation potential of this molecule, our assumption was that this proceeded through further reduction of an initial aryl radical to form an aryl anion.

Evidence in favour of an anion was seen when substrate **70** was used.[32] When this substrate was reacted with **64**, the indanone **71** was formed in 51% yield. Donor **64** also dehalogenated bromonaphthalenes and 9-chloroanthracene (not shown in Schemes here). Reaction of donor **64** with *p*-toluenesulfonamides was governed by the stabilisation of the nitrogen leaving group.[33] Reductive cleavage proceeded well (*e.g.* **73**→**74**) except for *N,N*-dialkyl *p*-toluenesulfonamides, when the leaving group would be a dialkylamide anion. Then, cleavage was not observed. In the reaction with *gem bis*-sulfones, *e.g.* **75**, reductive cleavage was observed in high yield, affording the sulfone-stabilised anion corresponding to **76**.[33] On workup, sulfone **76** was isolated.

The synthesis of the doubly bridged donor **64** was quite time-consuming, and required skilful fractional crystallisations. This was completely to do with the need to assemble a second trimethylene bridge, with the step **77**→**78**, but as Taton and Chen had shown,[30] any less rigid analogue *e.g.* the monobridged compound **63**, could not be prepared, with all approaches to **63** resulting in the dicarbene **79**. Accordingly, we proposed to move away from imidazole-derived donors and elected to try to form the DMAP-derived **81** (Scheme 9). The planned route would be analogous to that for forming the tetraazafulvalenes, requiring deprotonation of the easily formed **80** to form a pyridinylidene, followed by cyclisation and deprotonation. Given the difficulties in preparing the imidazole-derived donors, it was unclear if this compound would be stable. In the event, the compound **81** was a well behaved purple solid, with the expected sensitivity to air and moisture. Its cyclic voltammogram showed a two-electron reversible wave at a similar potential to that of **64**,[34] $E_{1/2}$ (DMF) = –1.69 V *vs*. Fc/Fc$^+$ [equivalent to –1.20 V *vs*. Ag/AgCl/KCl (sat)].

The two strongest super-electron-donors, **64** and **81**, showed a similar reactivity. Both formed aryl anions from iodoarenes. Indeed, reaction of donor **81** with iodoester **67** afforded a very good conversion to the indanone **68**. To facilitate isolation of **68**, the byproduct, deiodinated and uncyclised ester **72**, was hydrolysed to acid **82** (8%) allowing isolation of **68** (83%).[34] Weinreb amides (*e.g.* **83**)[35] and acyloin derivatives (*e.g.* **85**)[36] were also reduced efficiently by donor **81**.

The most surprising reactions of the strong donors **64** and **81** were those with alkyl halides.[37] For example, the alkyl bromide **87** was converted to the homologated aldehyde **88** on reaction with **64** in DMF, followed by acidic workup (Scheme 10). Initial thoughts that an alkyl anion was an intermediate following further reduction of **89**, and that formylation occurred



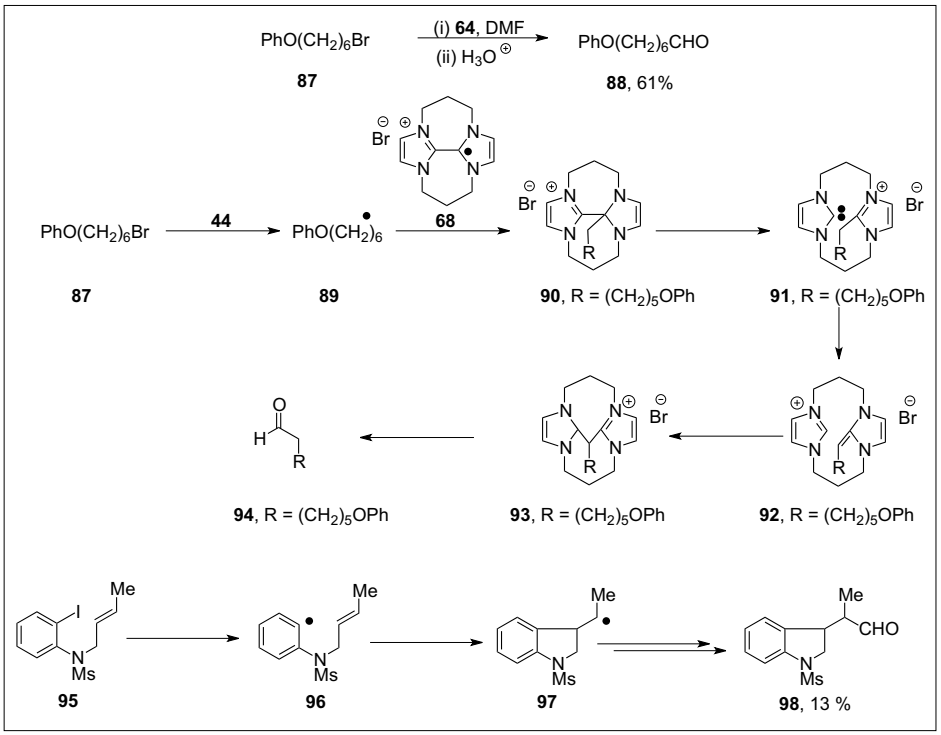
Scheme 9.

through nucleophilic attack upon DMF were discarded, when the same aldehyde product **88** emerged when dimethyl acetamide was used as solvent. Accordingly, the source of the aldehyde carbon must be the donor **64** itself or its oxidised forms, and Scheme 10 represents current thinking. Here **90** is the key intermediate; we propose its formation through combination of radical **89** and radical cation **68**. Although **90** could be produced by direct nucleophilic attack of **64** on bromide **87**, we have seen aldehydes produced from aryl halides such as in the conversion of **95** to **98**, which is very likely to proceed through formation and cyclisation of aryl radical **96** and trapping of the cyclised alkyl radical **97**. In the case of these aryl halides, the aldehyde is formed in lower yield, consistent with the main pathway being reduction of the aryl radical **96** to an aryl anion as discussed above (Schemes 8 and 9).

Returning to compound **90**, conversion to the aldehyde product **94** requires fragmentation of the central C–C bond and this could afford carbene **91**. Direct reduction of 2-alkylimidazolium salts by electron transfer was not observed in separate experiments in our work, and so we do not favour reduction of imidazolium salts like **91** as a route to the aldehyde. An alternative pathway would involve intramolecular deprotonation of the iminium salt in **91** by the carbene group. The resulting enamine in **92** could attack the imidazolium salt to afford **93**. Here the geminal diamine can easily be hydrolysed to an aldehyde group. In principle, the imidazolium salt in **93** could be hydrolysed to a carboxylic acid, although it would be a difficult reaction. If it were to occur, then decarboxylation would yield the observed aldehyde **94**.

Evidence for the iminium salt/enamine intermediates in this transformation was sought using the specially designed diether iodides **99**. If these form radicals that behave analogously to radical **89** in Scheme 10 then the carbene imidazolium salt **101** in Scheme 11 will play the part of **91** in Scheme 10. Intramolecular deprotonation would afford enediamine **102** which should expel the alkoxide RO^- in forming **103**. The same alkoxide could then deprotonate this vinylimidazolium salt to form diene-diamine **104**. This should now expel the second alkoxide $R'O^-$. When the experiments were conducted, the alcohols ROH and R'OH were liberated and isolated in good yield, for a range of substrates, consistent with enamine/iminium salt intermediates shown in the mechanistic proposal in Scheme 11.

Reviewing progress at this stage, strong neutral organic donors have been prepared and characterised and we have begun to explore their chemistry. Nevertheless, exciting challenges remain in determining the limits to reactivity for organic electron donors, and we look forward to continued participation in this quest.



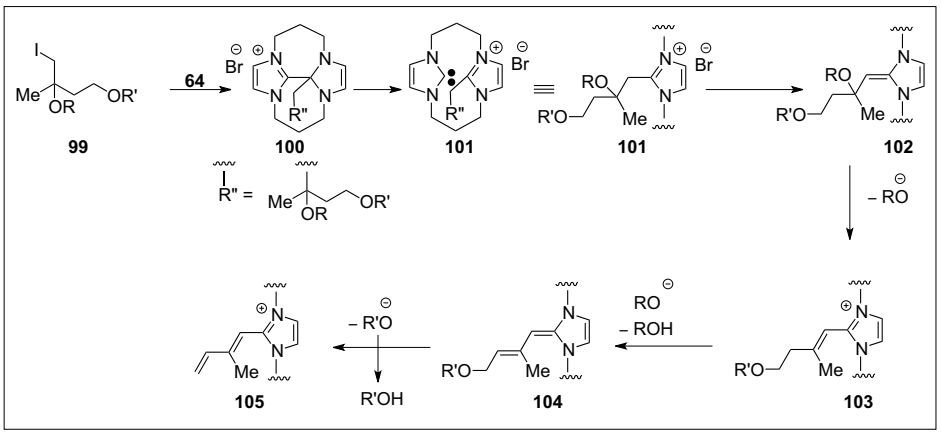
Scheme 10.

Acknowledgements

JM thanks his students and postdoctoral researchers, for their dedication and enthusiasm in helping to uncover the reactions of electron-rich organic molecules. We thank University of Strathclyde, WestCHEM, AstraZeneca and EPSRC for funding.

Received: February 25, 2012

[1] A. J. Birch, *Quart. Rev., Chem. Soc*. **1950**, *4*, 69.
[2] D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 76.
[3] F. Wudl, G. M. Smith, E. J. Hufnagel, *Chem. Commun*. **1970**, 1453.
[4] a) H. Prinzbach, H. Berger, A. Lüttringhaus, *Angew. Chem. Int. Ed*. **1965**, *4*, 435; b) A. Takamizawa, K. Hirai, *Chem. Pharm. Bull.* **1969**, *17*, 1931.
[5] P. R. Ashton, V. Balzani, J. Becher, A. Credi, M. C. T. Fyfe, G. Mattersteig, S. Menzer, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 3951.
[6] a) V. E. Kampar, G. V. Bumbure, V. R. Kokars, O. Ya. Neiland *Zh. Obshch. Khim*. **1980**, *50*, 2057 (for translation, see *J. Gen. Chem. U.S.S.R*. **1980**, *50,* 1663); b) V. R. Kokars, V. E. Kampar, O. Ya. Neiland *Zh. Org. Khim.* **1983**, *19*, 1224, (for translation, see *J. Org. Chem. U.S.S.R.* **1983**, *19*, 1092).
[7] a) C. Lampard, J. A. Murphy, N. Lewis, *J. Chem. Soc., Chem. Commun*. **1993**, 295; b) R. J. Fletcher, C. Lampard, J. A. Murphy, N. Lewis, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 623; c) J. A. Murphy, The radical-polar crossover reaction, in 'Radicals in Organic Synthesis', Eds. P. Renaud, M. P. Sibi, Wiley VCH, Weinheim, **2001**, Vol. 1, pp. 298–315.
[8] N. Bashir, J. A. Murphy, *Chem. Commun*. **2000**, 627.
[9] O. Callaghan, C. Lampard, A. R. Kennedy, J. A. Murphy, *J. Chem. Soc., Perkin Trans. 1* **1999**, 995.



Scheme 11.

[10] L. Pause, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **1999**, *121,* 7158.
[11] T. Jigami, K. Takimiya, T. Otsubo, Y. Aso, *J. Org. Chem.* **1998**, *63*, 8865.
[12] G. V. Tormos, M. G. Bakker, P. Wang, M. V. Lakshmikantham, M. P. Cava, R. M. Metzger, *J. Am. Chem.* Soc. **1995**, *117*, 8528.
[13] S. Hünig, D. Scheutzow, H. Schlaf, *Liebigs Ann. Chem*. **1972**, *765*, 126.
[14] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, R. H. Lafferty Jr., *J. Am. Chem.* Soc. **1950**, *72*, 3646.
[15] C. Burkholder, W. R. Dolbier, Jr., M. Médebielle, *Tetrahedron Lett.* **1997**, *38*, 821.
[16] For review of tetraazaalkenes, see N. Wiberg, *Angew. Chem. Int. Ed*. **1968**, *7*, 766.
[17] a) W. Carpenter, A. Haymaker, D. W. Moore, *J. Org. Chem.* **1966**, *31*, 789; b) W. Carpenter, Jr., *J. Org. Chem*. **1965**, *30*, 3082; c) M. W. Briscoe, R. D. Chambers, S. J. Mullins, T. Nakamura, J. F. S. Vaughan, F. G. Drakesmith, *J. Chem. Soc. Perkin Trans. 1* **1994**, 3115.
[18] a) C. Burkholder, W. R. Dolbier Jr., M. Médebielle, *J. Org. Chem.* **1998**, *63*, 5385; b) G. Giuglio-Tonolo, T. Terme, M. Médebielle, P. Vanelle, *Tetrahedron Lett.* **2003**, *44*, 6433; c) For a review of TDAE chemistry, see M. Médebielle, W.A. Dolbier, Jr. *J. Fluorine Chem*. **2008**, *129*, 930.
[19] M. Mahesh, J. A. Murphy, F. LeStrat, H. P. Wessel, *Beilstein J. Org. Chem*. **2009**, *5*, doi: 10.3762/bjoc.5.1.
[20] a) A. Peters, E. Kaifer, H.-J. Himmel, *Eur. J. Org. Chem*. **2008**, 5907; b) V. Vitske, C. König, O. Hübner, E. Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem*. **2010**, 115.
[21] T. P. Vaid, *J. Am. Chem. Soc.* **2011**, *133*, 15838.
[22] W. W. Porter III, T. P. Vaid, A. L. Rheingold, *J. Am. Chem Soc*. **2005**, *127*, 16559.
[23] Z. Han, T. P. Vaid, A. L. Rheingold, *J. Org. Chem.* **2008**, *73*, 445.
[24] J. R. Ames, M. A. Houghtaling, D. L. Terrian, T. P. Mitchell, *Can. J. Chem.* **1997**, *75*, 28.
[25] a) J. Bourson, *Bull. Soc. Chim. Fr*. 1971, 3541; b) S. Hünig, D. Scheutzow, H. Schlaf, H. Quast, *Liebigs Ann. Chem*. **1972**, *765*, 110; c) R. P. Thummel, V. Goulle, B. Chen, *J. Org. Chem*. **1989**, *54*, 3057; d) Z. Shi, R. P. Thummel, *J. Org. Chem*. **1995**, *60*, 5935.
[26] J. A. Murphy, T. A. Khan, S.-Z. Zhou, D. W. Thomson, M. Mahesh, *Angew. Chem. Int. Ed.* **2005**, *44*, 1356.
[27] J.-M. Savéant, *Acc. Chem. Res*. **1993**, *26*, 455.
[28] C. P. Andrieux, J. Pinson, *J. Am. Chem. Soc.* **2003**, *125*, 14801.
[29] M. D. Otero, B. Batanero, F. Barba, *Tetrahedron Lett.* **2006**, *47*, 8215.
[30] T. A. Taton, P. Chen, *Angew. Chem. Int. Ed. Engl*. **1996**, *35*, 1011.
[31] C. Heinemann, W. Thiel, *Chem. Phys. Lett*. **1994**, *217*, 11.
[32] J. A. Murphy, S.-Z. Zhou, D. W. Thomson, F. Schoenebeck, M. Mahesh, S. R. Park, T. Tuttle, L. E. A. Berlouis, *Angew Chem. Int. Ed*. **2007**, *46*, 5178.
[33] F. Schoenebeck, J. A. Murphy, S.-Z. Zhou, Y. Uenoyama, Y. Miclo, T. Tuttle, *J. Am. Chem. Soc*. **2007**, *129*, 13368.
[34] a) J. A. Murphy, J. Garnier, S. R. Park, F. Schoenebeck, S.-Z. Zhou, A. T. Turner, *Org. Lett*. **2008**, *10*, 1227; b) J. Garnier, J. A. Murphy, S.-Z. Zhou, A. T. Turner, *Synlett* **2008**, 2127; c) J. Garnier, A. R. Kennedy L. E. A. Berlouis, A. T. Turner, J. A. Murphy, *Beilstein J. Org. Chem*. **2010**, *6*, No. 73; d) R. Sword, L. A. Baldwin, J. A. Murphy, *Org. Biomol. Chem*. **2011**, *9*, 3560.
[35] S. P. Y. Cutulic, J A. Murphy, H. Farwaha, S.-Z. Zhou, E. Chrystal, *Synlett* **2008**, 2132.
[36] S. P. Y. Cutulic, N. J. Findlay, S.-Z. Zhou, E. J. T. Chrystal, J. A. Murphy, *J. Org. Chem.* **2009**, *74*, 8713.
[37] J. A. Murphy, F. Schoenebeck, N. J. Findlay, D. W. Thomson, S.-Z. Zhou, J. Garnier, *J. Am. Chem. Soc.* **2009**, *131*, 6475.