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Synthesis of Organic Super-Electron-Donors by Reaction of Nitrous Oxide with N-Heterocyclic Olefins

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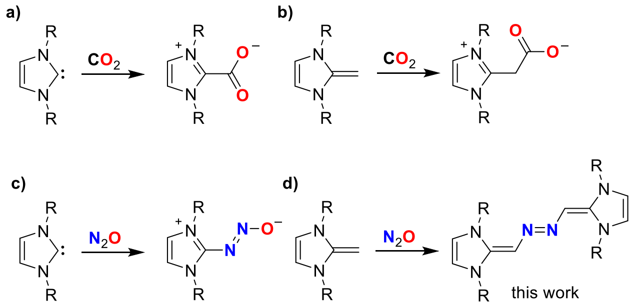
Supporting Information

ABSTRACT: The reaction of nitrous oxide (N_2O) with N-heterocyclic olefins (NHOs) results in cleavage of the N−O bond and formation of azo-bridged NHO dimers. The latter represent very electron-rich compounds with a low ionization energy. Cyclic voltammetry studies show that the dimers can be classified as new organic super-electron-donors, with a reducing power similar to what is found for tetraazafulvalene derivatives. Mild oxidants are able to convert the neutral dimers into radical cations, which can be isolated. Further oxidation gives stable dications.

N-heterocyclic carbenes (NHCs) are able to form covalent adducts with CO_2 (Scheme 1a).[1,2] The resulting imidazolium-2-carboxylates have been used as organocatalysts for different reactions,[3] and they represent easy-to-handle NHC transfer reagents for the synthesis of metal carbene complexes.[4]

Scheme 1. Reactions of NHCs and NHOs with CO_2 or N_2O



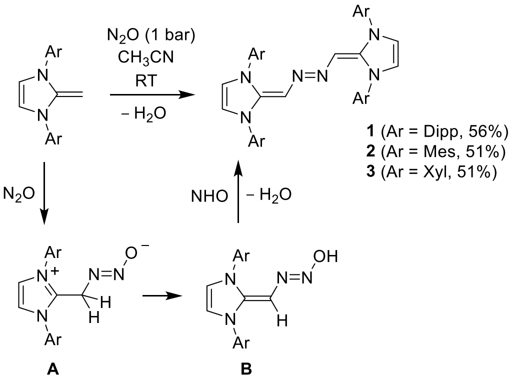
N-heterocyclic olefins (NHOs) are alkylidene derivatives of NHCs.[5] The exocyclic C=C double bond is strongly polarized, and the high charge density at the C_α atom makes NHOs strongly Lewis basic compounds. Similar to NHCs, NHOs react with CO_2 to give zwitterionic covalent adducts (Scheme 1b). These adducts are of key importance in CO_2 sequestration reactions with NHOs.[6]

Nitrous oxide (N_2O) is isoelectronic to CO_2 and likewise a chemically inert compound.[7] Despite its inert character, N_2O is able to form stable covalent adducts with NHCs under ambient conditions (Scheme 1c).[8] To date, NHC−N_2O adducts have not been used in the context of catalytic reactions, but they have been shown to act as mild and selective oxidants for metal complexes[9] and as precursors for azo dyes.[10]

The results summarized above prompted us to explore whether NHOs would also react with N_2O. Chemical activation of N_2O with NHOs can indeed be achieved under mild conditions. Instead of simple 1:1 adducts, we observed the formation of azo-bridged NHO dimers (Scheme 1d). These dimers represent new super-electron-donors, as evidenced by cyclic voltammetry and reactions with aryl iodides. Details of these investigations are given below.

For our studies, we used NHOs with 2,6-iPr$_2$C$_6$H$_3$ (Dipp), 2,4,6-Me$_3$C$_6$H$_2$ (Mes), and 2,6-Me$_2$C$_6$H$_3$ (Xyl) substituents.[11] When concentrated solutions of these compounds in CH_3CN were exposed to an atmosphere of N_2O, a gradual color change to orange/red was observed. After 48 h, strongly colored precipitates had formed (**1**−**3**; Scheme 2), which were isolated and washed with CH_3CN.

Scheme 2. Reaction of NHOs with N_2O



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The products displayed reduced symmetry compared with the starting NHOs, as evidenced by the presence of a double set of NMR signals for the *N*-aryl groups. This observation indicated that **1**−**3** are not simple NHO−N_2O adducts.

Analysis of **1** and **3** by single-crystal X-ray crystallography showed that azo-bridged NHO dimers had formed (for details, see the Supporting Information (SI)). The formation of these dimers can be rationalized by assuming that the reactions proceed via zwitterionic NHO−N_2O adducts of type **A** (Scheme 2), which can tautomerize to the diazohydroxides **B**.[12] A condensation reaction with remaining NHO then provides the dimers **1**−**3**. Presumably, the condensation reaction is initiated by N−O bond rupture of the diazohydroxide **B**, forming either a vinyl diazonium compound or a diazoalkene.[13]

Solutions of **1**−**3** in THF appear dark orange. The absorption in the visible range is in line with the solid-state structures of **1** and **3**, which both show a coplanar arrangement of the two heterocycles and the divinyldiazene bridge, allowing for efficient π conjugation. Linear-response time-dependent density functional calculations further confirm this observation, indicating for the main band of **1** a ππ* character located over the heterocycles and the divinyldiazene bridge (see the SI for computational details).

The reducing power of **1** was assessed by cyclic voltammetry (CH_3CN, 0.1 M NBu_4PF_6). Two well-separated reversible redox transitions were observed at $E_{1/2} = -1.34$ and -0.73 V, referenced versus an external Fc/Fc^+ redox couple. Similar values were obtained for the azo compounds **2** and **3** (see the SI). The first oxidation potential is comparable to what has been observed for some tetraazafulvalene derivatives, for example **C** and **D** (Figure 1), which are termed organic super-reducing agents.[14−17]

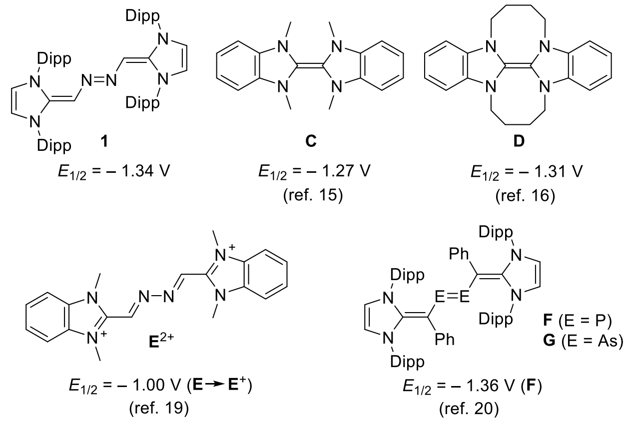


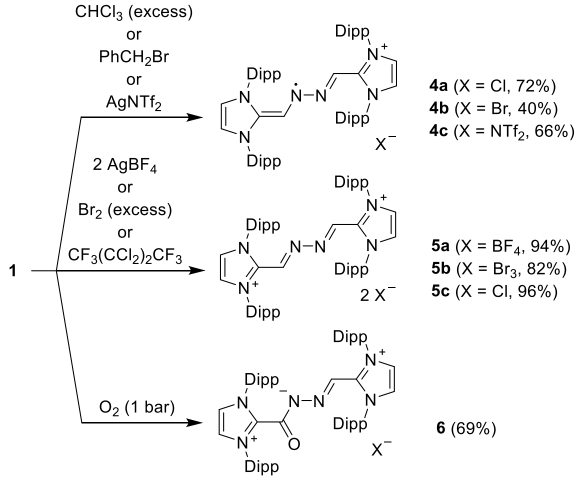
Figure 1. Redox potential for the first oxidation of **1** in comparison to the values for structurally related compounds reported in the literature. The values are based on CV measurements in CH_3CN (CH_2Cl_2 for **F**) with respect to the Fc/Fc^+ redox couple.[17]

Density functional theory (DFT) calculations using the ωB97X-D exchange−correlation functional[18] were performed to gain further insight into the electronic structure of the new compounds, using **1** as representative example (for details, see the SI). The calculations revealed a gas-phase vertical ionization energy (vIE) of 4.49 eV and an adiabatic ionization energy (aIE) of 4.16 eV. Inclusion of an implicit solvent model for CH_3CN in the calculation lowered the ionization energies to 4.19 eV (vIE) and 3.24 eV (aIE). Calculating the aIE of tetraazafulvalene derivative **C** using the same computational protocol (DFT/ωB97X-D/IEFPCM) gave a value of 3.34 eV, close to the one obtained for **1**.

It is worth discussing the structurally related compound $\mathbf{E}^{2+}$, **F**, and **G** (Figure 1). $\mathbf{E}^{2+}$ was described by Hünig and co-workers.[19] Electrochemical investigations showed that the corresponding neutral form **E** is formed at $E_{1/2} = -1.00$ V,[18] but isolation of the neutral compound was not attempted. The lower reducing power of **E** compared with **1** is likely related to the presence of annulated benzene rings.[14] The dipnictenes **F** and **G** were recently reported by Ghadwal and co-workers.[20] These compounds were obtained by reaction of phenyl-substituted NHOs with ECl_3 (E = P, As) followed by reduction. Electrochemical investigations of **F** indicated that the first oxidation occurs at $E_{1/2} = -1.36$ V.[20a]

The chemical reactivity of the new azo-bridged NHOs was investigated, again using compound **1** as a representative example. The large difference between the first and second oxidation potentials allows for selective one-electron oxidation of **1**. The oxidation can be accomplished using chloroform, benzyl bromide, or silver triflimide as the oxidant (Scheme 3). The resulting salts **4a**−**c** were isolated in yields between 40 and 72%.

Scheme 3. Reactions of 1 with Different Oxidants



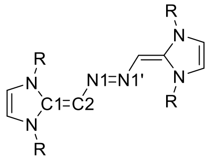
In the absence of air, the salts are stable in solution (THF) and in the solid state.[21] Crystallographic analyses of **4a**−**c** revealed that the single-electron oxidation resulted in lengthening of the C1−C2 and N1−N1′ bonds and shortening of the C2−N1 bond (Table 1).

The presence of a radical cation in **4** was confirmed by EPR spectroscopy (Figure 2a). The complex hyperfine coupling indicates that the radical is delocalized over the planar π system. Such delocalization is in accordance with the results of DFT calculations, which show that the spin density is distributed over the two heterocycles and the divinyldiazene bridge (Figure 2b).

Solutions of **4** are strongly colored, and the UV−vis spectrum (THF) shows absorption bands at 661 and 736 nm in addition to a main band at $\lambda_{max} = 516$ nm. The occurrence of low-energy bands is typical for π-conjugated radicals.[22]

The addition of 2 equiv of $AgBF_4$, an excess of bromine, or 2,2,3,3-tetrachlorohexafluorobutane to a solution of **1** resulted in the formation of imidazolium salts **5a**−**c**, which could be

Table 1. Selected Bond Lengths for 1, 3, 4a−c, and 5b As Determined by X-ray Crystallography[a]



compound	C1−C2	C2−N1	N1−N1′
1	1.3692(14)	1.3703(14)	1.2907(16)
3	1.3685(14)	1.3713(13)	1.2902(16)
4a	1.408(3)	1.324(2)	1.327(3)
4b	1.4108(18)	1.3214(17)	1.333(2)
4c	1.4109(15)	1.3237(14)	1.3300(18)
5b	1.450(3)	1.271(3)	1.400(3)

[a]All of the structures show a crystallographic inversion center.

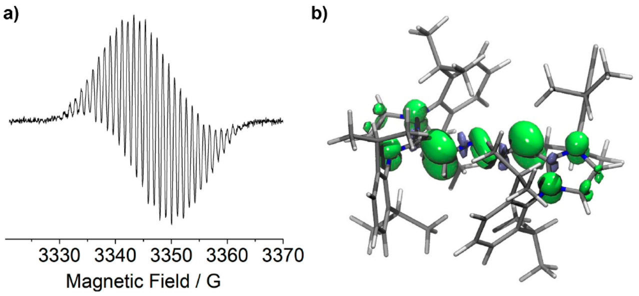


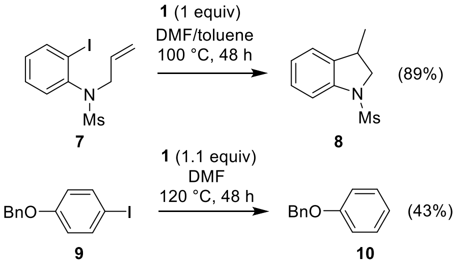
Figure 2. (a) EPR spectrum of **4a** and (b) calculated spin density of the radical cation.

isolated in high yields (Scheme 3). Crystallographic analysis of **5b** showed that the double oxidation led to further lengthening of the C1−C2 and N1−N1′ bonds and shortening of the C2−N1 bond (Table 1).

When a solution of **1** in a mixture of diethyl ether and hexane (2:1) was exposed to dioxygen, we observed the formation of a brown-yellow oily solid. Workup allowed isolation of the salt **6** in 69% yield (Scheme 3). As evidenced by mass spectrometry and single-crystal X-ray crystallography (see the SI), the reaction with O_2 resulted in oxidation of one of the C_α atoms of the azo-bridged dimer.[23]

To qualify as an organic super-reducing agent, a compound should be able to reduce aryl iodides.[14] We examined the reaction of **1** with aryl iodides **7** and **9** (Scheme 4).[24] When a solution of **7** and **1** in a mixture of DMF and toluene (1:1) was heated to 100 °C, cyclization to form indoline **8** was observed.[25] The latter could be isolated in 89% yield. The more challenging substrate **9** could also be reduced. However, (benzyloxy)benzene (**10**) was formed in only 43% yield, and incomplete conversion was observed.

Scheme 4. Reactions of Aryl Iodides with 1



In summary, we have examined the reaction of N-heterocyclic olefins with nitrous oxide. Instead of simple N_2O adducts, we observed N−O bond cleavage and formation of azo-bridged NHO dimers (**1**−**3**). These dimers are very strong electron donors, which can be converted into stable radical cations or a dicationic imidazolium salts. The first oxidation potentials are similar to what is observed for some tetraazafulvalenes, allowing the reduction of aryl iodides. Consequently, **1**−**3** can be classified as new super-electron-donors. Tetraazafulvalenes have been used as potent reducing agents in synthetic chemistry,[14] and similar applications can be envisioned for the new diazenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b10660.

Experimental details, analytical data, and supporting figures (PDF)
Crystallographic data for **1** (CIF)
Crystallographic data for **3** (CIF)
Crystallographic data for **4a** (CIF)
Crystallographic data for **4b** (CIF)
Crystallographic data for **4c** (CIF)
Crystallographic data for **4d** (CIF)
Crystallographic data for **5b** (CIF)
Crystallographic data for **6** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Song, H.; Kim, Y.; Park, J.; Kim, K.; Lee, E. Activation of Small Molecules at N-Heterocyclic Carbene Centers. *Synlett* **2016**, *27*, 477−485. (b) Wang, S.; Wang, X. Imidazolium Ionic Liquids, Imidazolylidene Heterocyclic Carbenes, and Zeolitic Imidazolate Frameworks for CO_2 Capture and Photochemical Reduction. *Angew. Chem., Int. Ed.* **2016**, *55*, 2308−2320. (c) Delaude, L. Betaine Adducts of N-Heterocyclic Carbenes: Synthesis, Properties, and Reactivity. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1681−1699.

(2) (a) Vogt, M.; Bennett, J. E.; Huang, Y.; Wu, C.; Schneider, W. F.; Brennecke, J. F.; Ashfeld, B. L. Solid-Sate Covalent Capture of CO_2 by Using N-Heterocyclic Carbenes. *Chem. - Eur. J.* **2013**, *19*, 11134−11138. (b) Van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. A Systematic Investigation of Factors Influencing the Decarboxylation of Imidazolium Carboxylates. *J. Org. Chem.* **2009**, *74*, 7935−7942. (c) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. Reversible carboxylation of N-heterocyclic carbenes. *Chem. Commun.* **2004**, 112−113. (d) Kuhn, N.; Steimann,

M.; Weyers, G. Synthesis and Properties of 1,3-Diisopropyl-4,5-dimethylimidazolium-2-carboxylate. A Stable Carbene Adduct of Carbon Dioxide. *Z. Naturforsch., B: J. Chem. Sci.* **1999**, *54*, 427−433.

(3) For selected examples, see: (a) Naumann, S.; Buchmeiser, M. R. Liberation of N-heterocyclic carbenes (NHCs) from thermally labile progenitors: protected NHCs as versatile tools in organo- and polymerization catalysis. *Catal. Sci. Technol.* **2014**, *4*, 2466−2479. (b) Lindner, R.; Lejkowski, M.; Lavy, S.; Deglmann, P.; Wiss, K. T.; Zarbakhsh, S.; Meyer, L. M.; Limbach, M. Ring-Opening Polymerization and Copolymerization of Propylene Oxide Catalyzed by N-Heterocyclic Carbenes. *ChemCatChem* **2014**, *6*, 618−625. (c) Hans, M.; Delaude, L.; Rodriguez, J.; Coquerel, Y. N-Heterocyclic Carbene Catalyzed Carba-, Sulfa-, and Phospha-Michael Additions with NHC·CO$_2$ Adducts as Precatalysts. *J. Org. Chem.* **2014**, *79*, 2758−2764. (d) Kayaki, Y.; Yamamoto, M.; Ikariya, T. N-Heterocyclic Carbenes as Efficient Organocatalysts for CO$_2$ Fixation Reactions. *Angew. Chem., Int. Ed.* **2009**, *48*, 4194−4197. (e) Zhou, H.; Zhang, W.-Z.; Liu, C.-H.; Qu, J.-P.; Lu, X.-B. CO$_2$ Adducts of N-Heterocyclic Carbenes: Thermal Stability and Catalytic Activity toward the Coupling of CO$_2$ with Epoxides. *J. Org. Chem.* **2008**, *73*, 8039−8044.

(4) (a) Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O.; Crabtree, R. H. Imidazolium Carboxylates as Versatile and Selective N-Heterocyclic Carbene Transfer Agents: Synthesis, Mechanism, and Applications. *J. Am. Chem. Soc.* **2007**, *129*, 12834−12846. (b) Tudose, A.; Demonceau, A.; Delaude, L. Imidazol(in)ium-2-carboxylates as N-heterocyclic carbene precursors in ruthenium-arene catalysts for olefin metathesis and cyclopropanation. *J. Organomet. Chem.* **2006**, *691*, 5356−5365. (c) Voutchkova, A. M.; Appelhans, L. N.; Chianese, A. R.; Crabtree, R. H. Disubstituted Imidazolium-2-carboxylates as Efficient Precursors to N-Heterocyclic Carbene Complexes of Rh, Ru, Ir, and Pd. *J. Am. Chem. Soc.* **2005**, *127*, 17624−17625.

(5) (a) Roy, M. M. D.; Rivard, E. Pushing Chemical Boundaries with *N*-Heterocyclic Olefins (NHOs): From Catalysis to Main Group Element Chemistry. *Acc. Chem. Res.* **2017**, *50*, 2017−2025. (b) Ghadwal, R. S. Carbon-based two electron σ-donor ligands beyond classical N-heterocyclic carbenes. *Dalton Trans.* **2016**, *45*, 16081−16095.

(6) (a) Zhou, H.; Wang, G.-X.; Lu, X.-B. CO$_2$ Adducts of α-Carbon Alkylated N-Heterocyclic Olefins: Highly Active Organocatalysts for CO$_2$ Chemical Transformation. *Asian J. Org. Chem.* **2017**, *6*, 1264−1269. (b) Crocker, R. D.; Nguyen, T. V. The Resurgence of the Highly Ylidic N-Heterocyclic Olefins as a New Class of Organocatalysts. *Chem. - Eur. J.* **2016**, *22*, 2208−2213. (c) Saptal, V. B.; Bhanage, B. M. N-Heterocyclic Olefins as Robust Organocatalysts for the Chemical Conversion of Carbon Dioxide to Value-Added Chemicals. *ChemSusChem* **2016**, *9*, 1980−1985. (d) Wang, Y.-B.; Sun, D.-S.; Zhou, H.; Zhang, W.-Z.; Lu, X.-B. CO$_2$, COS and CS$_2$ adducts of N-heterocyclic olefins and their application as organocatalysts for carbon dioxide fixation. *Green Chem.* **2015**, *17*, 4009−4015. (e) Wang, Y.-B.; Wang, Y.-M.; Zhang, W.-Z.; Lu, X.-B. Fast CO$_2$ Sequestration, Activation, and Catalytic Transformation Using N-Heterocyclic Olefins. *J. Am. Chem. Soc.* **2013**, *135*, 11996−12003.

(7) (a) Severin, K. Synthetic Chemistry with Nitrous Oxide. *Chem. Soc. Rev.* **2015**, *44*, 6375−6386. (b) Leont'ev, A. V.; Fomicheva, O. A.; Proskurnina, M. V.; Zefirov, N. S. Modern chemistry of nitrous oxide. *Russ. Chem. Rev.* **2001**, *70*, 91−104.

(8) (a) Tskhovrebov, A. G.; Vuichoud, B.; Solari, E.; Scopelliti, R.; Severin, K. Adducts of Nitrous Oxide and N-Heterocyclic Carbenes: Syntheses, Structures, and Reactivity. *J. Am. Chem. Soc.* **2013**, *135*, 9486−9492. (b) Göhner, M.; Haiss, P.; Kuhn, N.; Ströbele, M.; Zeller, K.-P. The 1:1 Adduct of 1,3-Diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene and Nitrous Oxide. *Z. Naturforsch., B: J. Chem. Sci.* **2013**, *68*, 539−545. (c) Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. Covalent Capture of Nitrous Oxide by N-Heterocyclic Carbenes. *Angew. Chem., Int. Ed.* **2012**, *51*, 232−234.

(9) (a) Falcone, M.; Barluzzi, L.; Andrez, J.; Fadaei Tirani, F.; Zivkovic, I.; Fabrizio, A.; Corminboeuf, C.; Severin, K.; Mazzanti, M. The role of bridging ligands in dinitrogen reduction and functionalization by uranium multimetallic complexes. *Nat. Chem.* **2019**, *11*, 154−160. (b) Palluccio, T. D.; Rybak-Akimova, E. V.; Majumdar, S.; Cai, X.; Chui, M.; Temprado, M.; Silvia, J. S.; Cozzolino, A. F.; Tofan, D.; Velian, A.; Cummins, C. C.; Captain, B.; Hoff, C. D. Thermodynamic and Kinetic Study of Cleavage of the N−O Bond of N-Oxides by a Vanadium(III) Complex: Enhanced Oxygen Atom Transfer Reaction Rates for Adducts of Nitrous Oxide and Mesityl Nitrile Oxide. *J. Am. Chem. Soc.* **2013**, *135*, 11357−11372. (c) Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. Sequential N-O and N-N Bond Cleavage of N-Heterocyclic Carbene-Activated Nitrous Oxide with a Vanadium Complex. *J. Am. Chem. Soc.* **2012**, *134*, 1471−1473.

(10) Tskhovrebov, A. G.; Naested, L. C. E.; Solari, E.; Scopelliti, R.; Severin, K. Synthesis of Azoimidazolium Dyes with Nitrous Oxide. *Angew. Chem., Int. Ed.* **2015**, *54*, 1289−1292.

(11) (a) Powers, K.; Hering-Junghans, C.; McDonald, R.; Ferguson, M. J.; Rivard, E. Improved synthesis of *N*-heterocyclic olefins and evaluation of their donor strengths. *Polyhedron* **2016**, *108*, 8−14. (b) Ibrahim Al-Rafia, S. M.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; McDonald, R.; Rivard, E. Intercepting low oxidation state main group hydrides with a nucleophilic N-heterocyclic olefin. *Chem. Commun.* **2011**, *47*, 6987−6989.

(12) Eymann, L. Y. M.; Scopelliti, R.; Fadaei Tirani, F.; Severin, K. Synthesis of Azo Dyes from Mesoionic Carbenes and Nitrous Oxide. *Chem. - Eur. J.* **2018**, *24*, 7957−7963.

(13) (a) Glaser, R.; Chen, G. S.; Barnes, C. L. Origin of the Stabilization of Vinyldiazonium Ions by β-Substitution; First Crystal Structure of an Aliphatic Diazonium Ion: β,β-Diethoxyethenediazonium Hexachloroantomonate. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 740−743. (b) Bott, K. Dialkylamino-substituierte Ethylendiazoniumsalze. *Chem. Ber.* **1987**, *120*, 1867−1871. (c) Bott, K. Alkenediazonium Salts: A New Chapter of Classical Organic Chemistry. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 259−265.

(14) (a) Murphy, J. A. Discovery and Development of Organic Super-Electron-Donors. *J. Org. Chem.* **2014**, *79*, 3731−3746. (b) Broggi, J.; Terme, T.; Vanelle, P. Organic Electron Donors as Powerful Single-Electron Educing Agents in Organic Synthesis. *Angew. Chem., Int. Ed.* **2014**, *53*, 384−413.

(15) Kamplain, J. W.; Lynch, V. M.; Bielawski, C. W. Synthesis and Study of Differentially Substituted Dibenzotetraazafulvalenes. *Org. Lett.* **2007**, *9*, 5401−5404.

(16) Shi, Z.; Thummel, R. P. N.N'-Bridged Derivatives of 2,2'-Bibenzimidazole. *J. Org. Chem.* **1995**, *60*, 5935−5945.

(17) The redox potentials of compounds **E** and **F** were measured using SCE or Ag/AgCl references, respectively. The potentials were converted to the Fc/Fc$^+$ scale using a conversion constant of 0.38 mV (SCE) or 0.40 mV (Ag/AgCl). See: Pavlishchuk, V. V.; Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. *Inorg. Chim. Acta* **2000**, *298*, 97−102.

(18) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.

(19) (a) Hünig, S.; Scheutzow, D.; Schlaf, H.; Pütter, H. Spectroscopy and Polarography of Vinylogous Bibenzimidazoles, Bibenzoxazole and Bibenzothiazoles and their Aza Derivatives. *Liebigs Ann. Chem.* **1974**, *1974*, 1436−1449. (b) Hünig, S.; Scheutzow, D.; Schlaf, H.; Schott, A. Synthesis of Vinylogous Benzimidazoles, Benzoxazoles and Benzothiazoles and their Aza Derivatives. *Liebigs Ann. Chem.* **1974**, *1974*, 1423−1435.

(20) (a) Sharma, M. K.; Rottschäfer, D.; Blomeyer, S.; Neumann, B.; Stammler, H.-G.; van Gastel, M.; Hinz, A.; Ghadwal, R. S. Diphosphene radical cations and dications with a π-conjugated C$_2$P$_2$C$_2$-framework. *Chem. Commun.* **2019**, *55*, 10408−10411. (b) Rottschäfer, D.; Sharma, M. K.; Neumann, B.; Stammler, H.-G.; Andrada, D. M.; Ghadwal, R. S. A Modular Access to Divinylphosphenes with a Strikingly Small HOMO-LUMO Energy Gap. *Chem. - Eur. J.* **2019**, *25*, 8127−8134. (c) Sharma, M. K.; Blomeyer, S.; Neumann, B.; Stammler, H.-G.; Ghadwal, R. S.

DOI: 10.1021/jacs.9b10660

Crystalline Divinyldiarsenes and Cleavage of the As = As Bond. *Chem. - Eur. J.* **2019**, *25*, 8249−8253.

(21) Investigation of the solids by quantitative EPR spectroscopy showed no noticeable decomposition after 1 week.

(22) Torrance, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. E. Optical properties of the radical cation tetrathiafulvalenium (TTF$^+$) in its mixed-valence and monovalence halide salts. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1979**, *19*, 730−741.

(23) For the structure of **7**, we observed disorder for the anion and for the cocrystallized solvent. The crystallographic data point to the presence of Cl$^-$ instead of the expected HO$^-$. Possibly, anion exchange occurred during the crystallization process (glassware).

(24) For reactions of these substrates with tetraazafulvalenes, see: (a) Jolly, P. I.; Zhou, S.; Thomson, D. W.; Garnier, J.; Parkinson, J. A.; Tuttle, T.; Murphy, J. A. Imidazole-derived carbenes and their elusive tetraazafulvalene dimers. *Chem.Sci.* **2012**, *3*, 1675−1679. (b) Murphy, J. A.; Khan, T. A.; Zhou, S.; Thomson, D. W.; Mahesh, M. Highly Efficient Reduction of Unactivated Aryl and Alkyl Iodides by a Ground-Sate Neutral organic Electron Donor. *Angew. Chem., Int. Ed.* **2005**, *44*, 1356−1360.

(25) A reaction between **7** and **1** in toluene at room temperature resulted in the precipitation of the radical cation ($\mathbf{1}^{\bullet+}$)(I$^-$) (**4d**), the structure of which was characterized by X-ray diffraction. For details, see the SI.