Photochemistry

Metal-Free C—C Coupling Reactions with Tetraguanidino-Functionalized Pyridines and Light

Simone Stang, Elisabeth Kaifer, and Hans-Jörg Himmel*^[a]

Abstract: Herein we report on metal-free C—C coupling reactions mediated by the pyridine derivative 2,3,6,7-tetrakis-(tetramethylguanidino)pyridine under the action of visible light. The rate-determining step is the homolytic N—C bond cleavage of the initially formed *N*-alkyl pyridinium ion upon excitation with visible light. The released alkyl radicals subsequently dimerize to the C—C coupling product. 2,3,6,7-Tetra-

Introduction

Photoinduced reactions involving pyridinium salts were intensively studied in the past. Hence, photoexcitation of a suitable electron donor molecule (sensitizer) was shown to lead to oneelectron reduction of N-alkoxy-pyridinium acceptors. A prerequisite for such an intermolecular electron transfer reaction is the formation of a charge-transfer complex, in which the donor and acceptor molecules generally establish π - π interactions. Gould et al. studied the mechanism for N-O bond cleavage of the resulting N-alkoxy-pyridinyl radical.^[1] Bending of the O atom from the alkoxy group out of the pyridinyl ring plane leads to mixing between σ^* and π^* orbitals, which is essential for a low barrier to N-O bond cleavage. The effect of electronwithdrawing and donating groups on the barrier was also studied and it was shown that the barrier is lowered by electron-donating groups attached to the radical.^[1] Such photoreactions have found important applications. The alkoxy radicals produced under light were used, for example, to initiate radical polymerization reactions.^[2] Furthermore, the chain-amplified photochemical fragmentation of N-alkoxypyridinium salts was applied in organic synthesis.[3]

Compared with *N*-alkoxy-pyridinyl radicals, *N*-alkyl-pyridinyl radicals are more stable,^[4] and CV experiments prove the reversible reduction of several *N*-alkyl-pyridinium salts.^[5] Consequently, up to date such compounds have found less applications. Kochi et al. reported photoreactions with pyridinium tetraalkylborate charge-transfer salts (some also react thermally)

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	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304987.

kis(tetramethylguanidino)pyridine, which is a strong electron donor ($E_{1/2}$ (CH₂Cl₂) = -0.76 V vs. ferrocene) is oxidized to the dication. For alkyl = benzyl and allyl, relatively high first-order rate constants of 0.23 ± 0.03 and 0.13 ± 0.03 s⁻¹ were determined. Regeneration of neutral 2,3,6,7-tetrakis(tetrame-thylguanidino)-pyridine by reduction allows to drive the process in a cycle.



Scheme 1. Example for a photoreaction involving an *N*-alkyl-pyridinium charge-transfer salt. The example shows at the same time the strength of the N–C bond, which remains intact.

such as that in Scheme 1.^[6] However, in this case the pyridinium-methyl bond remains intact, proving again its stability. In two fundamental publications, Katritzky, Eyler et al. studied the collisionally-activated dissociation of a series of *N*-alkylpyridinium ions in the gas phase.^[7] The products were either pyridine and alkyl cations or pyridinium ions and alkenes (see Scheme 2). They compared their experimental results with



Scheme 2. Collisionally activated gas-phase fragmentation of pyridinium ions.

Chem. Eur. J. 2014, 20, 5288 - 5297

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360 nm was assigned to the

Using density functional theory

311G**), the HOMO-LUMO gap was estimated to be 4.31 eV

(288 nm) in 1 and 3.38 eV

(367 nm), 3.48 eV (356 nm) and

3.35 eV (370 nm) in [1-Me]⁺,

[1-CH₂Ph]⁺ and [1-CH₂CH=CH₂]⁺,

calculations

excitation.^[8]

(B3LYP/6-

(see Figure 1a). The bond distances within the cationic unit are

in line with the resonance structures shown in Scheme 4a, indi-

cating delocalization of the positive charge into the guanidino

groups. Alkylation of 1 leads to a decrease of the HOMO-

LUMO gap. Consequently, the N-alkyl pyridinium salts are in-

tensively yellow colored. A strong band centered at 433 nm in

the UV/Vis spectrum of [1-CH₂Ph]⁺ can be assigned to the

HOMO \rightarrow LUMO transition (see Figure 2a and Figure S1 in the

Supporting Information for spectra of salts containing the

cation [1-CH₃]⁺), and this transition is clearly involved in the

photochemistry. In 1, a band at a significantly higher energy of

(DFT)

 $HOMO \rightarrow LUMO$

AM1 (Austin Model 1) calculations. With relevance to the work reported herein, they found that the reaction enthalpies for alkyl cation formation decrease in the order R=Me (410 kJ mol⁻¹) > H₂C=CH-CH₂ (213 kJ mol⁻¹) > PhCH₂ (172 kJ mol⁻¹). In the case of R=PhCH₂, the initially formed PhCH₂⁺ cation could subsequently rearrange to the more stable tropylium cation, leading to a further decrease of the reaction enthalpy to 126 kJ mol⁻¹.

We recently reported the synthesis of the pyridine derivative 2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)pyridine, **1** (see Scheme 3), which turned out to be a strong organic electron



Scheme 3. Metal-free photocoupling reaction of alkyl halides (R = benzyl or allyl in this work) with 2,3,5,6-tetra-kis(1,1,3,3-tetramethylguanidino)-pyridine, 1, as discussed in this work. No reaction was observed for the related electron donor 1,2,4,5-tetrakis(1,1,3,3-tetramethylguanidino)-benzene, 2.

a)

Me₂]

Meab

Me₂N

Me₂N

donor with $E_{1/2}(CH_2CI_2) = -0.76 V$ vs. Fc/Fc^+ (Fc = ferrocene) for two-electron oxidation.[8] Oxidation is fully reversible. Herein we show that visible-light irradiation of solutions of 1-alkyl-2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)-pyridinium salts, formed from 1 and alkyl halides) leads to C-C coupling reactions. Such reactions are not feasible for other pyridinium salts, and might pave the way for the broader usage of 1 in metal-free photochemical C--C coupling reactions. The related compound 2 (1,2,4,5-tetrakis(1,1,3,3-tetrame-

respectively. Hence, the calculations predict correctly a decrease Me₂ NMe₂ NMe₂ Me₂] Me₂ NMe₂ Me₂N ·NMe₂ Me₂N NMe ·NMe₂ Me₂N -NMe₂ Me₂N NMe . NMe₂ NMe₂ Me Me₂N Me₂ b) Me₂N NMe₂ -NMe Me₂N

NMe

NMe-

Scheme 4. a) Resonance structures for $[1-R]^+$ showing the delocalization of the positive charge into the guanidino groups. b) Lewis structure of the trication $[1-R]^{3+}$.

Me₂N=

Me₂N

thylguanidino)benzene, see Scheme 3),^[9] which is similar to **1** in its redox potential, does not mediate C–C coupling reactions. In this work we focus on some aspects of the mechanism of this new photoreaction.

Results and Discussion

Alkylation of 1

The first step in the C–C coupling reaction with **1** is the formation of an alkyl-pyridinium salt. Therefore we started our work with the preparation of the *N*-benzyl, *N*-allyl or *N*-methyl pyridinium salts of compound **1** by reaction between **1** and one equivalent of alkyl (benzyl, allyl, or methyl) halide or triflate (trifluoromethane-sulfonate, O_3SCF_3). The structure of the salt [**1**-Me]I in the solid state was determined by X-ray diffraction of the HOMO-LUMO gap upon alkylation (73 nm according to experiment versus 68 nm according to the calculations for benzyl), and only the absolute values deviate. The HOMO energy decreases upon alkylation of 1, reducing the electron donor capacity. Hence the CV curves show a shift by 0.23 V towards higher potentials for the first (two-electron) oxidation waves upon alkylation (with benzyl). Nevertheless, [1-CH₂Ph]⁺ still is a strong electron donor, and [1-CH₂Ph]Br can readily be oxidized, for example, with I_2 to give the salt $[1-CH_2Ph]Brl_{1.5}(I_3)_{0.5}$. The structures of the trications $[1-CH_3]^{3+}$ and [1-CH₂Ph]³⁺ as derived from an X-ray diffraction analysis are displayed in Figure 1 b and c. In the trication [1-CH₃]³⁺, the short distances N1-C1 and N10-C5 (1.276(3) and 1.287(3) Å) together with the long N1-C7 and N10-C22 bond distances argue for localization of two positive charges mainly on the two guanidino groups next to the N ring atom. The third posi-



Figure 1. Structures of a) The [1-Me]⁺ cation in the salt [1-Me]I, b) the $[1-Me]^{3+}$ trication in the salt $[1-Me](F_3CSO_3)_3$, and c) the $[1-CH_2C_6H_5]^{3+}$ trication in the salt $[1-CH_2C_6H_5]BrI_{1.5}(I_3)_{0.5}$ (hydrogens omitted). Vibrational ellipsoids drawn at the 50% probability level. Selected bond distances (in Å) for [1-Me]⁺: N1-C1 1.377(10), N1-C7 1.345(12), N2-C7 1.360(11), N3-C7 1.362(13), N4-C2 1.410(11), N4-C12 1.306(11), N5-C12 1.375(11), N6-C12 1.372(11), N7-C4 1.393(11), N7-C17 1.278(13), N8-C17 1.392(13), N9-C17 1.397(11), N10-C5 1.335(11), N10-C22 1.337(11), N11-C22 1.354(11), N12-C22 1.345(12), N13-C1 1.325(11), N13-C5 1.389(10), N13-C6 1.493(10), C1-C2 1.422(12), C2-C3 1.388(12), C3-C4 1.419(12), C4-C5 1.401(11). Selected bond distances (in Å) for [1-Me]3+: N1-C1 1.276(3), N1-C7 1.385(3), N2-C7 1.323(3), N3-C7 1.334(3), N4-C2 1.300(3), N4-C12 1.390(3), N5-C12 1.326(3), N6-C12 1.329(3), N7-C4 1.336(3), N7-C17 1.351(3), N8-C17 1.345(3), N9-C17 1.344(3), N10-C5 1.287(3), N10-C22 1.378(3), N11-C22 1.346(3), N12-C22 1.333(3), N13-C1 1.381(3), N13-C5 1.377(3), N13-C6 1.478(3), C1-C2 1.503(3), C2-C3 1.405(3), C3-C4 1.370(3), C4-C5 1.500(3). Selected bond distances (in Å) for $[1\text{-}CH_2C_6H_5]^{3+}\text{:}$ N1–C1 1.281(6), N1–C6 1.378(6), N2-C6 1.336(6), N3-C6 1.344(6), N4-C2 1.317(6), N4-C11 1.377(6), N5-C11 1.338(6), N6-C11 1.327(6), N7-C4 1.316(6), N7-C16 1.373(6), N8-C16 1.327(6), N9-C16 1.349(6), N10-C5 1.294(6), N10-C21 1.380(6), N11-C21 1.332(6), N12-C21 1.336(6), N13-C1 1.370(6), N13-C5 1.378(5), N13-C26 1.474(6), C1-C2 1.505(6), C2-C3 1.382(6), C3-C4 1.394(6), C4-C5 1.495(6).

tive charge is delocalized in the "other half" (1,3-bisguanidinoallyl) of the molecule (see the Lewis structure in Scheme 4b). A similar electronic situation is found for $[1-CH_2Ph]^{3+}$. The dihedral angle between the "CN₂ plane" of the C(NMe₂)₂ group of each guanidino substituent and the plane of the central heterocycle remains large, most likely for steric reasons. Solutions of $[1-R]^{3+}$ are, like solutions of 1^{2+} , red-colored. When solutions





Figure 2. a) Comparison between the UV/Vis spectra of 1 and $[1-CH_2Ph]^+Br^-$. b) Illustration of the isodensity surfaces of HOMO and LUMO in $[1-CH_2Ph]^+$ (B3LYP/6-311G** calculations). The H atoms were omitted for clarity.

of $[1-R]^+$ were stored for some time under sun light, a color change from yellow to red signaled a light-induced redox process. A small number of red-colored crystals of $[1-Me]Tf_3$ and $[1-CH_2Ph]Br_3$ were isolated from [1-Me]Tf and $[1-CH_2Ph]Br$ solutions exposed to sun light for several days (see Figure S2 in the Supporting Information and the Experimental Section). These results were the first hints of an interesting photochemistry.

The isodensity surfaces of the HOMO and LUMO orbitals of $[1-CH_2Ph]^+$ are visualized in Figure 2 b (B3LYP/6-311G** calculation). The pyridinium ring orbitals, but also the guanidino group orbitals contribute to the HOMO and LUMO. In addition, it can be seen that in the LUMO the benzyl group is also involved. This mixing between the π^* orbital of the pyridine ring with guanidino and benzyl orbitals is of importance for the observed photochemistry. It is also worth mentioning that both the UV/Vis spectra (measured at various concentrations) as well as the crystal structure data show no sign for the formation of a charge-transfer complex, in which the alkylated 1 would be electron donor and acceptor at the same time (see below).

Photochemistry

Solutions of the pyridinium salts in CH₃CN were then irradiated with a 150 W medium-pressure Hg lamp, either in a quartz glass cuvette or in a Schlenk flask. The behavior was very different for $[1-CH_2Ph]^+$ and $[1-CH_3]^+$. In the case of $[1-CH_2Ph]^+$, a fast photoreaction was observed, while $[1-CH_3]^+$ reacts very slowly. After 15 min of irradiation of a $1.76 \cdot 10^{-5}$ M solution of





Figure 3. a) Photo of a solution of $[1-CH_2C_6H_3]^+Br^-$ in CH_3CN (2.47·10⁻⁵ M) before (left) and after irradiation with a Hg high pressure lamp (150 W) for 15 min. b) UV/Vis spectra of a $[1-CH_2C_6H_5]^+Br^-$ solution in CH_3CN for different irradiation times. c) Plot of the absorption intensity at 513 nm as a function of the irradiation time together with an exponential fit.

[1-CH₂Ph]⁺Br⁻ in CH₃CN in a guartz glass cuvette, the solution had changed color from yellow to red (see photo in Figure 3 a), and the spectroscopic data signaled completion of the reaction. UV/Vis spectra recorded after different irradiation times are shown in Figure 3b. The absorptions due to [1-CH₂Ph]⁺ at 433 and 340 nm completely vanished, and new absorptions at 513 (broad) and 369 nm appeared. The spectra clearly showed that all of the [1-CH₂Ph]⁺ cations were consumed after 15 min. Isosbestic points were located at 475 and 400 nm, indicating formation of a single product with absorptions in the visible region. The photoproduct can be identified unambiguously as the dication $1^{2+[8]}$ The trication $[1-CH_2Ph]^{3+}$, which exhibits bands at 492 and 358 nm with a different intensity ratio, can be ruled out. Due to the large half-width of the bands, it could in principal be formed as side product, but the presence of clear isosbestic points shows that its concentration can only be very small. The isolation of a few number of [1-CH₂Ph]Br₃ crystals upon expose of solutions of [1-CH₂Ph]Br to sunlight for several days is therefore the result of an equilibrium $([1-CH_2Ph]^++1^{2+}\leftrightarrow [1-CH_2Ph]^{3+}+1)$ which lies on the left side, but leads to formation of some [1-CH₂Ph]³⁺ if only a small amount of 1^{2+} is present. The absorption intensity at 513 nm was plotted as a function of irradiation time, and the data could be fitted satisfactorily by an exponential function (see Figure 3 c), in line with a first-order kinetics with a rate constant k of approximately (0.23 ± 0.03) min⁻¹. The reaction was repeated with different concentrations of [1-CH₂Ph]⁺Br⁻. An increase in the concentration from $1.76 \cdot 10^{-5}$ M to $2.47 \cdot 10^{-5}$ M did not affect the k value. On the other hand, a further increase to $3.36 \cdot 10^{-5}$ M led to a slightly reduced reaction rate. In this case the reaction was completed in ca. 20 min. These results can be explained by the reduction of light intensity by absorption. Prolonged irradiation times led in all cases to a secondary reaction and bleaching of the solution. The absorptions at 513 (broad) and 369 nm vanished and absorptions at 241, 270, and 341 nm (the latter with a shoulder at 370 nm) appeared (Figure 4). However, the absence of isosbestic points in this

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Figure 4. Effect of prolonged irradiation of a solution of $[1-CH_2C_6H_5]^+Br^-$ in CH₃CN (2.47·10⁻⁵ M) with broadband light. The dication 1^{2+} , which is formed after 30 min of photolysis, is consumed after 480 min irradiation.

second photoreaction signaled a more complex process that might lead to product mixtures. The results demonstrate that prolonged photolysis times, at least with broadband light, have to be avoided.

Figure 5 shows the UV/Vis spectra recorded under similar conditions for a $1.84 \cdot 10^{-5}$ M solution of $[1-CH_3]^+I^-$ in CH_3CN . The concentration lies in the low-concentration region which should allow the determination of the rate constant. It can be seen that the photoreaction proceeds significantly slower, and even after 360 min of irradiation with broadband light about 50% of the $[1-CH_3]^+$ ions remained. After 30 min of photolysis, the appearance of new absorptions indicated formation of 1^{2+} in small quantities. However, as already observed in the case of the reaction with $[1-CH_2Ph]^+Br^-$, longer irradiation times did not lead to an increase of the dication concentration, since it is itself consumed in a slow photoreaction.

Subsequently, we repeated the experiments with a $2.7\cdot10^{-5}$ M solution of the allyl-pyridinium salt [1-CH₂-CH=



Figure 5. UV/Vis spectra recorded for $[1-Me]^+I^-$ solutions $(1.84 \cdot 10^{-5} \text{ M})$ in CH₃CN in dependence of the photolysis time.

CH₂]⁺Br⁻ in quartz glass cuvettes. From the experience with [1-CH₂Ph]⁺Br⁻ we kept the concentration low to avoid deceleration of the reaction rate due to self-absorption effects (the UV/Vis spectra collected in our experiments are shown in Figure S3 in the Supporting Information). Again, the presence of isosbestic points indicated a clean photoreaction in the first minutes of irradiation, which leads to the same product, namely the dication 1^{2+} . After 20 min of irradiation, all [1-CH₂-CH=CH₂]⁺ ions had reacted. A plot of the absorption intensity versus irradiation time (see Figure S4 in the Supporting Information) argues for a first-order kinetics, in agreement with the results obtained with the benzyl compound. However, the reaction rate was in the case of $[1-CH_2-CH=CH_2]^+Br^-$ (0.13 \pm 0.03 min⁻¹) slightly lower than for $[1-CH_2Ph]^+Br^-$ (0.23 \pm 0.03 min⁻¹). In full agreement with the other experiments, prolonged irradiation times led to a decrease of the absorptions due to 1^{2+} (Figure S5 in the Supporting Information).

Then we carried out the photoreaction with $[1-CH_2Ph]^+Br^$ in Schlenk flasks and with higher concentrations of the reactant. Under these conditions, longer irradiation times of 2 h were necessary to complete the reaction. Using GC/MS, the second species, besides 1^{2+} , generated under the action of the light was identified as the carbon–carbon coupling product PhCH₂CH₂Ph. An overall reaction equation, which is in agreement with the experimental findings, is given in Scheme 5. Ac-

$$2 [\mathbf{1} - \mathbf{R}]^{+} \xrightarrow{h\nu} \mathbf{1}^{2+} + \mathbf{1} + \mathbf{R} - \mathbf{R}$$
$$[\mathbf{1} - \mathbf{R}]^{+} + \mathbf{R} - \mathbf{R} \xrightarrow{h\nu} \mathbf{1}^{2+} + \mathbf{B} - \mathbf{r}^{-} + \mathbf{R} - \mathbf{R}$$

Scheme 5. Photoreaction of $[1-R]^+$ without and with addition of RBr (R = benzyl).

cording to this equation, it should be possible to increase the yield of 1,2-diphenylethane by addition of one equivalent of benzyl bromide, which reacts with 1 to give further photoactive $[1-CH_2Ph]^+$. This was indeed the case. Broadband photolysis of an equimolar mixture of PhCH₂Br and $[1-CH_2Ph]^+$ gave 1,2-diphenylethane in a yield of up to 60% (with respect to



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Figure 6. Plot of the GC/MS measurements and photos before and after irradiation of a $[1-CH_2C_6H_5]^+Br^-$ solution in CH_3CN (4.7·10⁻³ M) for a period of 120 min.

benzyl). In Figure 6, the consumption of PhCH₂Br and the generation of the coupling product PhCH₂CH₂Ph (measured with GC/MS) are plotted together as a function of the irradiation time. From this plot it can be seen that prolonged irradiation times did not decrease the amount of PhCH₂CH₂Ph, meaning that the product is not involved in the second slower photoreaction in which 1^{2+} is consumed. Up to an irradiation time of ca. 150 min, the only species detected with GC/MS were the coupling product PhCH₂CH₂Ph and the reactant PhCH₂Br. Neutral 1, $[1^{2+}](Br^{-})_2$ and $[1-CH_2Ph]^+Br^-$ got stuck on the column. After 150 min of irradiation, 60% of the PhCH₂Br reactant molecules had reacted to the desired product, leaving 40% of the initial PhCH₂Br molecules in solution. The UV/Vis spectra showed already at this stage complete consumption of all [1-CH₂Ph]⁺ ions. Longer photolysis times did not improve the yield of the couple product, and only led to a slow decrease in the number of reactant molecules. At the same time, the formation of small amounts of benzaldehyde was detected via GC/MS. Since we excluded H₂O or O₂ rigorously, we think that the oxygen stems from reactions of the radicals produced by irradiation (see below) with the glass walls of the reaction vessel. In addition, another side reaction must occur to explain the presence of significant amounts of unreacted PhCH₂Br. Since the alkylation of 1 proceeds quantitatively at room temperature, this side reaction must cause the loss of some of the formed neutral molecules of 1. This point is addressed below.

The same results as with a mixture of $[1-CH_2Ph]^+$ and PhCH₂Br were obtained when mixtures of 1 and two equivalents of PhCH₂Br were irradiated. On the other hand, in experiments in which 1 was replaced by 2, which is comparable in

Chem. Eui	r. J. 2	014 , 20,	5288 – 5297	
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its reduction potential,^[9] no reaction occurred. This result clearly shows that fast electron transfer from the organic donor to the alkyl is only possible if a bond is established (resembling in this aspect the "inner-sphere" mechanism for electron transfer in transition metal chemistry). In further experiments, we irradiated a solution containing $[1-CH_2Ph]^+$ and allyl bromide (C₃H₅Br) in an equimolar ratio. The C–C coupling products were 1,2-diphenylethane (PhCH₂CH₂Ph) and 4-phenyl-1-butene (PhCH₂CH₂CH=CH₂), which were formed in a 2:1 molar ratio. 1,5-Hexadiene (H₂C=C(H)CH₂CH₂CH=CH₂) was not found. Similarly, irradiation of mixtures of [1-CH₂CH=CH₂]⁺ and PhCH₂Br only produced 1,5-hexadiene and 4-phenyl-1-butene, but no 1,2-diphenylethane. All these results clearly show that irradiation leads to the cleavage of the pyridine N-C alkyl bond in the first place. They also indicate that cross coupling reactions (and maybe more effective ring-closing reactions) are possible.

In another experiment, we irradiated a solution of $[1-CH_2Ph]^+Br^-$ with the 465 and 488 nm lines of an Ar⁺ ion laser. In both cases the photoreaction took place, but it was faster with the 465 nm line, which is close in energy to the absorption maximum (at 433 nm) of the band assigned to the HOMO-LUMO excitation in the UV/Vis spectrum. This result argues for photodissociation of [1-CH₂Ph]⁺ directly upon photoexcitation of an electron into the LUMO. An alternative mechanism, which would involve excitation into the LUMO+1 or higher energetic orbitals and electron transfer to another [1-CH₂Ph]⁺ ion to produce a neutral [1-CH₂Ph]⁺ radical species which subsequently dissociates, could be excluded on this basis. This alternative mechanism would resemble the reduction of N-alkoxy-pyridinium salts after electron transfer from an excited electron donor molecule,^[1] with the specialty that [1-CH₂Ph]⁺ acts simultaneously as electron donor and acceptor component. Such a mechanism is presumably only feasible if the donor and the acceptor component could form a charge-transfer complex, which is clearly not the case with [1-CH₂Ph]⁺. The proposed radical pathway sketched in

$[1-\mathbf{R}]^+ \xrightarrow{h\nu} \{[1-\mathbf{R}]^+\}^*$				
Chosen Pathway	Excluded			
$\{ [1-R]^+ \}^* \longrightarrow 1^+ \cdot + R \cdot$	$\{[1-R]^+\}^* + [1-R]^+ \longrightarrow [1-R]^{2+*} + [1-R]^*$			
$2 1^+ \cdot \longrightarrow 1^{2+} + 1$	$2 [1-R]^{2+} \rightarrow [1-R]^{3+} + [1-R]^{+}$			
	[1 -R] • → 1 + R •			
2 R • — — R — R				
$1 + RX \longrightarrow [1-R]^+ + X^-$				

Scheme 6. Pathway of the photoreaction between $\left[1\text{-}R\right]^+$ and RX (e.g., $R\!=\!CH_2Ph).$

Scheme 6 also involves disproportionation of the radical cation 1^{++} into 1^{2+} and 1. This disproportionation is supported by CV experiments showing the first and second electron oxidation from 1 to occur at the same potential.^[8,10] Unfortunately, we were not able to trace the radicals by EPR spectroscopy, most

likely because they are subjected to fast reactions. The first-order kinetics indicates that the cleavage of the N–C bond by light is the rate-determining step.

We carried out quantum chemical calculations (B3LYP/ 6-311G**) to compare the gas-phase N-C bond fragmentation of the N-benzyl pyridinium ion with that of the cation [1-CH₂Ph]⁺. According to our calculations, the formation of alkyl cations by heterolytic N-C bond cleavage is associated with a change of the Gibbs free energy (298 K, 1 bar) of +156 kJ mol⁻¹. By contrast, the homolytic N–C bond cleavage leading to alkyl radicals is strongly disfavored $(\Delta G = +327 \text{ kJmol}^{-1})$. As mentioned in the Introduction, collisionally induced N-C fragmentation of N-alkyl pyridinium ions in the gas phase leads to formation of alkyl cations,^[7] a result which is in good agreement with our calculations. In the case of [1-CH₂Ph]⁺, the situation changes drastically (see Scheme 7). Hence, the pathway leading to the benzyl radical (homolytic N-C bond fragmentation) is now preferred. It is associated with a relatively low ΔG value of +73 kJ mol⁻¹. On the other hand, alkyl cation formation is highly endergonic ($\Delta G = +306 \text{ kJmol}^{-1}$). Is the energy of the excited state of [1-R]⁺ higher than the energy needed for homolytic N–C bond fragmentation? To obtain a preliminary answer to this question, we assumed the lowest-energy triplet state to be similar to the open-shell first-excited singlet state. Indeed, the SOMOs of the triplet state agree nicely with the HOMO and LUMO of the singlet ground-state (Figure S6 in the Supporting Information). Under this assumption, the energy difference between the excited state and the ground state can be estimated by calculating the singlet-triplet energy difference. The triplet state of [1-CH₂Ph]⁺ exhibits a Gibbs free energy which is $172 \ \text{kJ} \, \text{mol}^{-1}$ higher than that of the singlet ground state. This implies that N-C bond fragmentation after photoexcitation is exergonic by approximately 100 kJ mol⁻¹. This estimate takes into account relaxation of the excited state prior to bond fragmentation. If one purely considers the light energy pumped into the $[1-CH_2Ph]^+$ cation (433 nm or 276 kJ mol⁻¹), it can be seen that the energy balance even allows for a barrier to fragmentation in the order of 100 kJ mol⁻¹ (if the energy is not ingested otherwise). In summary, these calculations lend strong support to the proposed pathway (see Scheme 6 and Scheme 7).

HOMO \rightarrow LUMO excitations generally involve mainly the π -system of the pyridine ring in the case of *N*-alkyl pyridinium ions ($\pi \rightarrow \pi^*$ transition).^[1] However, the π -system is orthogonal to the σ -bond between the pyridine N and the attached R. In the case of *N*-alkoxy-pyridinyl radicals, the resulting high barrier for N–O bond cleavage is reduced or vanishes completely (barrierless fragmentation) by bending of the N–C bond out of the pyridinyl ring plane.^[1] This bending allows mixing between π and σ orbitals. Our quantum chemical calculations (B3LYP/6-311G**) did not find evidence for a bending of the N–C bond out of the ring plane in the singlet or triplet state of the cation [1-CH₂Ph]⁺. On the other hand, the frontier orbitals of the [1-CH₂Ph]⁺ ion are clearly not purely π orbitals, but involve also the guanidino groups. Moreover, the illustration of the isodensity surface of the LUMO (see Figure 2b and Figure S6 in



NMe-

Scheme 7. N–C bond cleavage reactions showing the preference of *N*-alkyl pyridinium ions for alkyl cation formation. By contrast, 1-alkyl cations prefer to form alkyl radicals. The energies are ΔG values (1 bar, 198 K) for R=benzyl from B3LYP/6-311G** calculations.

the Supporting Information) also shows contributions from the benzyl group. Overall, the mixing between the pyridine π orbitals with guanidino and benzyl orbitals leads to a symmetry reduction and a lower barrier.

To obtain information about possible side reactions, which could explain that some of the added alkyl bromide did not react, we made several test experiments. In one of these experiments, we irradiated solutions of 1 in CH₃CN without addition of any alkyl bromide, and indeed observed the red-coloring of the solution after some time. The UV/Vis spectra (Figure S7 in the Supporting Information) clearly showed relatively slow photoinduced oxidation of 1 to give 1^{2+} (at least four times slower than the photoinduced N-C bond fragmentation of [1-CH₂Ph]⁺Br⁻). Such a photoinduced oxidation of 1 was not observed in THF solutions. Unfortunately, $1^{2+}(Br^{-})_{2}$ turned out to be poorly soluble in THF. Therefore, when the photoreaction between [1-CH₂Ph]⁺ and PhCH₂Br was repeated in THF solution, clouding of the solution by the formed solid $1^{2+}(Br^{-})_{2}$ particles reduced the transmittance of the reaction mixture and consequently led to a deceleration of the photoreaction. Nevertheless, these results show that an undesired side reaction involving the solvent can be avoided. In a continuousflow reactor the solution could be filtered so that the formation of solid particles should not represent a problem, and the reaction rate should increase considerably.^[11,12]

There are some reports in the literature of alkyl radical formation upon irradiation of alkyl halide solutions, however without evaluation of the mechanism (see the critical discussion in Ref. [13]). Under our experimental conditions, irradiation of alkyl halide solutions had no measurable effect. Also, the addition of pyridine to an alkyl halide solution did not initiate any photoreaction. Only if the pyridine derivative **1** was added, a photoreaction occurred. Photochemical generation of alkyl radicals from alkyl halides is also possible with metal complexes, especially cobalt complexes. A photolabile metal–alkyl complex is formed in the first step. Hence, it was shown that the Co–C bond in alkyl-cobaloximes (see Equation (a) in Scheme 8) could be cleaved by irradiation.^[14] In other work, the Co-C bond of benzyl complexes was cleaved homolytically either thermally or by photolysis to give benzyl radicals which dimerize to 1,2-diphenylethane.[15] A higher yield of 1,2-diphenylethane and a cleaner reaction was achieved by addition of an equivalent of benzyl bromide. Recently the reduction of benzyl bromide to give 1,2-diphenylmononuclear ethane via а cobalt-benzyl complex, anchored to semiconductor (TiO₂) nanocrystallites, has also been achieved photocatalytically.^[16] The TiO₂ material trapped and stored the electrons needed for reduc-

tion and enabled a multielectron transfer chemistry. Other metal complexes which were used to produce alkyl radicals from alkyl halides are $Mn_2(CO)_{10}^{[17]}$ and $[CpFe(CO)_2]_2$ (see Equations (b) and (c) in Scheme 8).^[18] The reduction of 1^{2+} allows the regeneration of 1,^[8, 19] so that the metal-free photocoupling process with 1 can be driven in a cycle. This cycle is visualized in Figure 7. At the present stage, the regeneration in the last step of this cycle must be carried out separately, and consequently stoichiometric amounts of the photosensitizer and reducing agent 1 are necessary. In ongoing research in our laboratory we are testing cheap reducing agents which could be added directly to the reaction mixture, and which might allow the development of metal-free photocatalytic coupling reactions with 1 as photocatalyst.



Scheme 8. Some metal complexes that were used in the past to generate alkyl radicals.

Chem. Eur. J. 2014, 20, 5288 – 5297



Figure 7. Cycle for C–C photocoupling reactions with 1.

Conclusion

In this work we report metal-free photocoupling reactions of alkyl halides with the compound 2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)pyridine (1), which is both photosensitizer and reducing agent. The mechanism of this reaction was studied, and shown to follow a radical pathway. In the first step, an N-alkyl-pyridinium salt is formed. Test experiments with related guanidine electron donors show that the formation of the N-C bond is essential. Then, irradiation with visible light leads in the rate-determining step to homolytic cleavage of the N-C bond. The guanidino groups turn the pyridine into a strong electron donor and weaken the N-C bond. In quantum chemical calculations the pyridine derivative 1 was compared with the parent pyridine, and the differences were highlighted which make such reactions possible with 1, but not with other known pyridines. The reaction rate was determined for the Nbenzyl-pyridinium and N-allyl-pyridinium ions ($k = 0.23 \pm 0.03$ and $0.13 \pm 0.03 \text{ s}^{-1}$). In the case of the *N*-methyl-pyridinium ion, the reaction was much slower. The resulting alkyl radicals dimerize to give the C-C coupling product. The radical monocation 1^{+} disproportionates to give 1^{2+} and 1. If the photoreaction is conducted at low concentration with a 1:2 molar ratio of 1 and the alkyl halide, 1 is completely consumed and the only products are the C-C coupling product and a salt of the dication 1^{2+} . If the reaction is repeated with higher concentrations, a yield of the photocoupling product to 60% in CH₃CN solutions was obtained, and the analysis disclosed ways to further increase the yield. Regeneration of neutral 1 by reduction of the dication formed in the course of the reaction offers the possibility to drive the process in a cycle. Ongoing experiments aim at the reduction of 1^{2+} directly in the reaction mixture, and at the development of metal-free photocatalytic coupling reactions with compound 1. We also briefly discussed first tests for cross-coupling reactions. In ongoing experiments we examine the suitability of 1 in photoinitiated ring-closing reactions. In summary, we think that 1 is an extremely interesting reagent for metal-free reductive photocoupling reactions. The present fundamental study stimulates more research in this field.

Experimental Section

All reactions were carried out under inert gas atmosphere using standard Schlenk techniques. The solvents were rigorously dried prior to their use. However, we recognized that the presence of water traces has no measurable influence on the photochemistry reported herein. Although 2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)pyridine (1) is a strong Brønsted base,^[8] the basicity is significantly reduced in the [1-R]⁺, ion which is rapidly formed upon alkylation. It especially turned out to be not necessary to dry the applied alkyl halides. Benzyl bromide (98%), allyl bromide (99%), methyl iodide (99.5%), and methyl triflate (98%) were purchased from Sigma-Aldrich and used as delivered. Compound 1 was synthesized as described previously.^[8] Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. UV/Vis measurements were carried out on a Cary 5000 spectrophotometer. Infrared spectra were recorded using a BIORAD Excalibur FTS 3000. NMR spectra were taken on a BRUKER Avance III 600, a BRUKER Avance II 400 or on a BRUKER Avance DPX AC200 spectrometer. Bruker ApexQe FT-ICR (ESI) and JEOL JMS-700 (HR-EI) machines were used for mass spectrometry (MS). Irradiation was achieved with a 150 W medium pressure Hg lamp (Heraeus TQ 150) as well as with the 465 or 488 nm lines of an Ar^+ ion laser (at 0.3 W, Coherent).

1-methyl-2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)pyridinium iodide, [1-Me]I

Compound 1 (51.0 mg, 0.096 mmol), was dissolved in 16 mL Et₂O. Then 7 µL of CH₃I (16.0 mg, 0.113 mmol) were added. The reaction mixture was stirred at room temperature for a period of 3 h. During this time, a deep-yellow colored solid precipitated. The solvent was removed under vacuum and the remaining solid washed three times with 3 mL portions of Et₂O. Subsequently the product was dried under vacuum yielding 64.4 mg (0.095 mmol, 99%). Crystals suitable for an X-ray diffraction analysis were obtained from $CH_2CI_2/Et_2O = 2:1$ solvent mixtures. ¹H NMR (400 MHz, CD_3CN): $\delta\!=\!6.03$ (s, 1H, H $_{\rm py}$), 3.77 (s, 3H, pyridine N-Me), 2.73 (s, 24H, NMe₂), 2.62 ppm (s, 24H, NMe₂); ¹³C NMR (100 MHz, MeCN), HSQC, HMBC: $\delta\!=\!$ 163.77 (s, C_{imino,guanidino}), 160.50 (s, C_{imino,guanidino'}), 145.82 (s, $C_{\rm py}$ (bonded to guanidino')), 131.11 (s, $C_{\rm py}$ (bonded to guanidino)), 123.91 (d, C_{py}), 39.85 (q, NMe₂), 39.74 (q, NMe₂), 35.83 ppm (q, Me (bonded to pyridine N)); UV/Vis (CH₃CN, $c = 1.97 \cdot 10^{-5} \text{ mol L}^{-1}$, d =1.0 cm): λ (nm, ε in Lmol⁻¹ cm⁻¹) = 425 (2.0·10⁴), 333 (1.4·10⁴), 246 (4.3·10⁴); HRMS (ESI⁺): *m/z* calcd (%): 546.44632; found: 546.44662 ([1-Me]⁺, 100%); elemental analysis calcd (%) for $C_{26}H_{52}N_{13}I$ (673.35): C 46.35, H 7.78, N 27.03; found C 46.45, H 7.67, N 26.92; crystal data for $C_{26}H_{52}IN_{13}$: Mr = 673.71, $0.30 \times 0.20 \times 0.15$ mm³, triclinic, space group *P*1, *a* = 14.697(3), *b* = 16.453(3), *c* = 17.291(4) Å, $\alpha = 114.78(3)^{\circ}$, $\beta = 97.10(3)^{\circ}$, $\gamma = 111.63(3)^{\circ}$, V = 3332(2) Å³, Z = 4, $d_{\text{calcd}} = 1.343 \text{ Mg} \cdot \text{m}^{-3}$, $\text{Mo}_{\text{K}\alpha}$ radiation (graphite monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.28 to 27.52°. Reflections measured; 26948, indep. 15062, $R_{int} = 0.0646$. Final *R* indices [$l > 2\sigma(l)$]: $R_1 = 0.0605, wR_2 = 0.1900.$



$\label{eq:2.3.5.6} 1-methyl-2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino) pyridinium triflate, [1-Me](O_3SCF_3)$

12.8 µL of methyl triflate (18.5 mg, 0.113 mmol) was slowly added at a temperature of 0 °C to a solution of 50.0 mg of 1 (0.094 mmol) in 16 mL Et₂O. The reaction mixture turned yellow and a deeplyyellow solid precipitated. After stirring the mixture at room temperature for a period of 1 h, the solvent was removed and the remaining solid washed 3 times with 3 mL portions of Et₂O. Then the solid was dried under vacuum to obtain 49.5 mg (0.071 mmol, 76%) of [1-Me](O₃SCF₃). ¹H NMR (400 MHz, CD₂Cl₂): δ = 5.95 (s, 1 H, H_{pv}), 3.79 (s, 3H, Me (bonded to pyridine)), 2.73 (s, 24H, NMe₂), 2.62 ppm (s, 24H, NMe₂); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 162.94 (s, $C_{\text{imino}}),\ 160.15$ (s, $C_{\text{imino}}),\ 145.30$ (s, C_{py} (bonded to guanidino)), 131.35 (s, C_{DV} (bonded to guanidino)), 123.86 (d, C_{DV}), 39.88 (q, NMe₂), 39.81 (q, NMe₂), 35.83 ppm (q, Me (bonded to pyridine N)); HRMS (ESI⁺): *m*/*z* calcd: 546.44632 found: 546.44685 ([LMe]⁺, 100 %); UV/Vis (CH₃CN, $c = 1.95 \cdot 10^{-5}$ mol L⁻¹, d = 0.5 cm): λ (nm, ϵ in Lmol⁻¹ cm⁻¹):426 (2.3·10⁴), 334 (1.2·10⁴), 250 (2.6·10⁴) (shoulder); elemental analysis calcd (%) for C₂₇H₅₂N₁₃SO₃F₃ (695.40): C 46.60, H 7.53, N 26.17; found: C 45.97, H 7.22, N 25.37.

1-allyl-2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)pyridinium bromide, [1-CH₂CH=CH₂]Br

8.1 µL of allyl bromide (11.4 mg, 0.094 mmol) were added to a solution of 50.0 mg of 1 (0.094 mmol) in 16 mL Et₂O. The reaction mixture was stirred for a period of 16 h under exclusion of light at room temperature, resulting in the precipitation of a deeply-yellow colored solid. The solvent was removed, the solid residue washed three times with portions of 5 mL Et₂O and the product subsequently dried under vacuum. Yield: 38.9 mg (0.06 mmol, 64%). ¹H NMR (600 MHz, MeCN): δ = 6.01–6.08 (m, 1 H, (CH)_{allvl}), 6.00 (s, 1 H, H_{py}), 5.19–5.24 (dd, ${}^{2}J = 21.4$ Hz, ${}^{3}J = 13.8$ Hz, 2 H, (CH₂)_{allyl}), 5.08 (d, J=5.8 Hz, 2 H, N-(CH₂)_{allyl}), 2.73 (s, 24 H, NMe₂), 2.62 ppm (s, 24 H, NMe_2); ^{13}C NMR (150 MHz, MeCN): $\delta\!=\!$ 163.32 (s, C_{\text{imino}}), 160.62 (s, $C_{imino}),\ 145.19$ (s, C_{py} (bonded to guanidino)), 133.29 (d, $(CH)_{allyl}),$ 130.57 (d, C_{py} (bonded to guanidino)), 124.32 (d, C_{py}), 119.02 (t, (CH₂)_{allyl}), 50.49 (t, N-(CH₂)_{allyl})), 39.89 (q, NMe₂), 39.80 ppm (q, NMe₂); HRMS (ESI⁺): *m*/*z* calcd: 572.46197; found: 572.46256 ([1-CH₂CH=CH₂]⁺, 100%); UV/Vis (CH₃CN, $c = 2.7 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$, d =1.0 cm): λ (nm, ϵ in Lmol⁻¹ cm⁻¹) = 432 (1.5·10⁴), 336 (1.4·10⁴), ca. 254 (2.5·10⁴), 219 (4.0·10⁴); elemental analysis calcd (%) for C₂₈H₅₄N₁₃Br (651.38): C 51.52, H 8.34, N 27.90; found: C 50.78, H 8.34, N 27.16;

1-benzyl-2,3,5,6-tetrakis(1,1,3,3-tetramethylguanidino)pyridinium bromide, [1-CH $_2C_6H_5$]Br

10.7 μ L C₆H₅CH₂Br (16.1 mg, 0.094 mmol) were added to a solution of 50.0 mg of 1 (0.094 mmol) in 16 mL Et₂O. The reaction mixture was stirred for a period of 4 h at room temperature, leading to precipitation of a deeply yellow-colored solid. After partial removal of the solvent the solution was cooled to 0 °C for 10 min before the remaining solvent was removed. The solid was washed three time with portions of 5 mL Et₂O and subsequently dried under vacuum. Yield: 53.5 mg (0.076 mmol, 81%). ¹H NMR (600 MHz, MeCN): δ = 7.48 (d, 2 H, H_{phenyl,ortho}), 7.32 (t, 2 H, H_{phenyl,meta}), 7.24(t, 1 H, H_{phenyl,para}), 6.01 (s, 1 H, H_{py}), 5.69 (s, 2 H, (CH₂)_{benzyl}), 2.64 (s, 24 H, NMe₂), 2.62 ppm (s, 24 H, NMe₂); ¹³C NMR (100 MHz, MeCN): δ = 163.59 (s, C_{imino,guanidino}), 161.23 (s, C_{imino,guanidino}), 145.75 (s, C_{py} (bonded to guanidino)), 130.57 (d, C_{phenyl,ortho}), 129.45 (d, C_{phenyl,meta}), 128.69 (d, C_{phenyl,ortho}), 129.50 (d, C_{phenyl,ortho}), 40.27 (q, NMe₂),

40.24 ppm (q, NMe₂); HRMS (ESI⁺): *m/z*: 622.4 ([1-CH₂C₆H₅]⁺, 100%), 311.7 ([1-CH₂C₆H₅]²⁺, 5.15%); UV/Vis (CH₃CN, *c* = 2.48·10⁻⁵ molL⁻¹, *d*=0.5 cm): λ (nm, ε in Lmol⁻¹ cm⁻¹)=433 (1.6·10⁴), 340 (1.3·10⁴), 261 (2.4·10⁴), 217 (4.9·10⁴); elemental analysis calcd (%) for C₃₂H₅₆N₁₃Br·2H₂O (701.40): C 52.02, H 8.19, N 24.65; found: C 52.59, H 8.12, N 24.24.

$[1-CH_2C_6H_5]BrI_{1.5}(I_3)_{0.5}$

10 mg of [1-CH₂C₆H₅]Br (0.017 mmol) were dissolved in 2 mL CH_3CN . Then 8.6 mg of I_2 (0.034 mmol) were added. The reaction mixture turned deep-red, and red-colored crystals precipitated after addition of 2 mL Et₂O. ¹H NMR (200 MHz, CD₃CN): δ = 7.45– 7.39 (m, 5H, H_{phenyl}), 5.51(s, 2H, CH_2), 4.94 (s, 1H, H_{Py}), 3.04 (s, 24H, NMe₂), 2.92 ppm (s, 24 H, NMe₂); ¹³C NMR (150 MHz, CD₃CN): $\delta =$ 166.38 (s, C_{imino}), 165.52 (s, C_{imino}), 150.76 (s, C_{py} (bonded to guanidino)), 149.68 (s, C_{phenyl} (bonded to CH_2)), 136.13 (s, C_{py} (bonded to guanidino)), 129.54 (d, C_{phenyl,para}), 129.53 (d, C_{phenyl,meta}), 128.28 (d, $C_{phenyl,ortho}$), 96.90 (d, C_{py}), 51.39 (t, (CH₂)_{benzyl}) 42.23 (q, NMe₂), 42.04 ppm (q, NMe₂); HRMS (ESI⁺): *m/z*: 207.8 ([1-CH₂C₆H₅]³⁺, 50.9%), 265.8 ([1]²⁺, 100%); UV/Vis (CH₃CN, $c = 1.29 \cdot 10^{-5} \text{ mol L}^{-1}$, d = 1 cm): λ (nm, ϵ in Lmol⁻¹ cm⁻¹) = 492 (0.5 \cdot 10^4), 358 (2.9 \cdot 10^4), 291 $(5.6 \cdot 10^4)$, 242 $(2.5 \cdot 10^4)$; Crystal data for $C_{32}H_{56}BrI_3N_{13}$: Mr = 1083.51, $0.25 \times 0.20 \times 0.20$ mm³, triclinic, space group *P*1, *a* = 11.498(2), *b* = 12.040(2), c = 16.808(3) Å, $\alpha = 89.12(3)^{\circ}$, $\beta = 70.07(3)^{\circ}$, $\gamma = 76.34(3)^{\circ}$, Å, V=2120.2(7) Å³, Z=2, d_{calc} =1.697 Mg·m⁻³, Mo_{Ka} radiation (graphite monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.32 to 33.00°. Reflections measured: 51044, indep: 15952, R_{int}=0.0597; final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0568$, $wR_2 = 0.1458$.

[1-Me](O₃SCF₃)₃ and [1-CH₂C₆H₅]Br₃

The compounds $[1-Me](O_3SCF_3)_3$ and $[1-CH_2C_6H_5]Br_3$ crystallized in small amounts from solutions of $[1-Me](O_3SCF_3)$ and $[1-CH_2C_6H_5]Br$ kept in the sun light for several days.

[1-Me](O₃SCF₃)₃

Crystal data for $C_{29}H_{52}F_9N_{13}O_9S_3$: Mr = 994.02, $0.40 \times 0.35 \times 0.30$ mm³, orthorhombic, space group P_{bcar} a = 18.629(4), b = 16.001(3), c = 28.986(6) Å, V = 8640(3) Å³, Z = 8, $d_{calc} = 1.528$ Mg m⁻³, Mo radiation (graphite monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 1.41 to 27.91°; Reflections measured: 20662, indep: 10314, $R_{int} = 0.0337$; final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0473$, $wR_2 = 0.1168$.

$[1\text{-}CH_2C_6H_5]Br_3$

Crystal data for $C_{32}H_{56}Br_3N_{13}$: Mr = 862.63, $0.30 \times 0.15 \times 0.15$ mm³, triclinic, space group $P\bar{1}$, a = 10.853(2), b = 11.957(2), c = 17.633(4) Å, $\alpha = 76.95(3)^{\circ}$, $\beta = 77.13(3)^{\circ}$, $\gamma = 78.93(3)^{\circ}$, V = 2148.8(7) Å³, Z = 2, $d_{calc} = 1.333$ Mg m⁻³, Mo_{Ka} radiation (graphite monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 1.94 to 27.53°; Reflections measured: 18427, indep: 9840, $R_{int} = 0.0663$; final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0602$, $wR_2 = 0.1288$.

X-ray crystallographic study

Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed on top of a glass capillary. Measurements were made with a Nonius-Kappa CCD diffractometer with low-temperature unit using graphite-monochromated $Mo_{K\alpha}$ radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.^[20] All calculations were performed using the SHELXT-PLUS software

Chem. Eur. J. 2014, 20, 5288 - 5297



package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.^[21,22] Graphical handing of the structural data during solution and refinement was performed with XPMA.^[23] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations. CCDC 976076 ([1-Me]I), 976080 ([1-CH₂C₆H₅]BrI_{1.5}(I₃)_{0.5}), 976079 ([1-Me](O₃SCF₃)I(I₅)), 976078 ([1-Me](O₃SCF₃)₃), and 976077 ([1-CH₂C₆H₅]Br₃) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical calculations

The GAUSSIAN 09 program was used for all calculations.^[24] Density functional theory (DFT) calculations were carried out with the B3LYP functional^[25] in combination with a 6–311G^{**} basis set.^[26] The calculated structures were similar to those determined by X-ray diffraction (see Table S1 for a comparison in the case of $[1-Me]^+$). To check the influence of the size of the basis set, the 6–31G^{*} basis set was also applied (Table S2). Moreover, we repeated the calculations with the pure DFT functional BP86 (Table S3). The results were similar.

Acknowledgements

The authors gratefully acknowledge continuous financial support from the Deutsche Forschungsgemeinschaft (DFG).

Keywords: C–C coupling · guanidine · photoreactions · radicals · reduction

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Received: December 20, 2013 Published online on March 27, 2014