Communications

# Nucleophilic Addition

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# Autocatalytic Carbonyl Arylation through In Situ Release of Aryl Nucleophiles from *N*-Aryl-*N'*-Silyldiazenes

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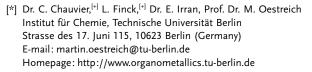
In memory of Rolf Huisgen and dedicated

to Professor Reinhard Brückner on the occasion of his 65th birthday

**Abstract:** A method for the catalytic generation of functionalized aryl alkali metals is reported. These highly reactive intermediates are liberated from silyl-protected aryl-substituted diazenes by the action of Lewis basic alkali metal silanolates, resulting in desilylation and loss of  $N_2$ . Catalytic quantities of these Lewis bases initiate the transfer of the aryl nucleophile from the diazene to carbonyl and carboxyl compounds with superb functional-group tolerance. The aryl alkali metal can be decorated with electrophilic substituents such as methoxycarbonyl or cyano as well as halogen groups. The synthesis of a previously unknown cyclophane-like [4]arene macrocycle from a 1,3-bisdiazene combined with a 1,4-dialdehyde underlines the potential of the approach.

Synthetic chemistry without aryl nucleophiles based on lithium, magnesium (Grignard), and zinc is difficult to imagine.<sup>[1]</sup> The usual methods for their preparation include reductive metalation and halogen-metal exchange of aryl halides, and the resulting polar organometallic reagents can be interconverted by transmetalation. These procedures are not always chemoselective, and the high reactivity of the nucleophiles is often detrimental to their functional-group tolerance. In particular, Knochel and co-workers have provided viable solutions to these problems, thereby turning polyfunctionalized zinc and Grignard reagents into everyday chemicals.<sup>[2-4]</sup>

An alternative to these reactive compounds are easy-tohandle and storable less polarized aryl pronucleophiles based on silicon, mainly the trimethylsilyl derivatives.<sup>[5]</sup> Aside from the fact that these are typically accessed from one of the aforementioned reagents, their fluoride- or alkoxide-promoted activation for aryl transfer to aldehydes is only applicable to electron-deficient aryl groups attached to the

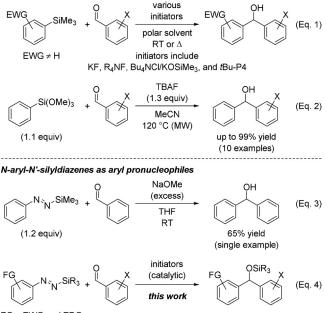


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silicon atom;<sup>[6]</sup> even the parent Ph-SiMe<sub>3</sub> does not react<sup>[6e,7]</sup> (Scheme 1, Eq. 1). This gap was closed with the more electrophilic Ph-Si(OMe)<sub>3</sub> and Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> (TBAF) as the Lewis basic activator (Scheme 1, Eq. 2).<sup>[8]</sup> To overcome this limitation, we considered the related activation of N-aryl-N'silvldiazenes (Ar-N=N-SiR<sub>3</sub>), which can be readily synthesized in two steps from arvl hydrazines with no need for arvl halides.<sup>[9]</sup> We envisioned that Lewis base activation of Ar-N= N-SiR<sub>3</sub> could unleash a reactive aryl nucleophile equivalent by desilylation and denitrogenation. This conceptual framework was formulated by Bottaro forty years ago (Scheme 1, Eq. 3), yet with no demonstration of its synthetic value and using NaOMe as an overstoichiometric activator.<sup>[10]</sup> This seminal contribution has been largely overlooked and, hence, has not witnessed any further development. The present work shows how this approach can be turned into a catalytic

### Aryl-substituted silanes as aryl pronucleophiles



FG = EWG and EDG

**Scheme 1.** Silicon-based aryl pronucleophiles in transition-metal-free 1,2-addition to aldehydes (alcohols after hydrolysis). EWG = electronwithdrawing group, EDG = electron-donating group, FG = functional group, X = aryl substituent. MW = microwave irradiation, R = alkyl or aryl group, tBu-P4 = 3-*tert*-butylimino-1,1,1,5,5,5-hexakis(dimethylamino)-3-{[[tris(dimethylamino)phosphoranylidene]amino}-1 $\lambda^5$ ,3 $\lambda^5$ ,5 $\lambda^5$ -1,4-triphosphazadiene (Schwesinger base), TBAF = tetrabutylammonium fluoride.

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process with excellent functional-group tolerance with respect to both the diazene and the carbonyl compound, including transformations of a difunctional building block (Scheme 1, Eq. 4).

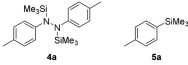
We began our investigation by testing various initiators in the reaction of 4-tolyl-substituted diazene 1a and benzaldehyde (2a) in THF (Table 1). Lithium salts such as the alkoxide tBuOLi  $[pK_a (H_2O) \approx 16.5]$  and the less basic silanolate Me<sub>3</sub>SiOLi<sup>[11]</sup> [ $pK_a$  (H<sub>2</sub>O)  $\approx$  12.7] both initiated the reaction at room temperature, affording the silyl ether 3aa in high yields within one hour (entries 1 and 2). With the same initiator loading of 10 mol%, improved reaction kinetics were achieved with the sodium and potassium salts of trimethylsilanol;[11] full conversion was reached in less than five minutes, accompanied by vigorous evolution of N<sub>2</sub> (entries 3 and 4). The same outcome was obtained with 5.0 mol% Me<sub>3</sub>SiONa but yields dwindled with 1.0 mol % Me<sub>3</sub>SiONa or Me<sub>3</sub>SiOK even at prolonged reactions times (entries 5-7). These results emphasize the influence of the alkali metal cation in this reaction. Polar co-solvents such as N-methylpyrrolidone (NMP) accelerated the already fast reactions. For completion, we included fluoride sources such as CsF and anhydrous TMAF into our screening. CsF did promote the aryl transfer but with a low reaction rate (entry 8), while essentially no conversion was seen with the poorly soluble ammonium fluoride (entry 9).

It is important to note that hydrazine 4a was never detected by GLC analysis in those experiments. This would arise from the addition of the aryl nucleophile across the N=N double bond of the diazene followed by silvlation.<sup>[12]</sup> This result suggests that the aldehyde substrate outcompetes the diazene as the electrophile. The silvlated arene 5a, which formally arises from the silvlation of the corresponding aryl anion, did usually form in trace amounts, likely because of the

Table 1:	Selected	examples from	the	optimization.
		0		initiator

	N <sub>≦N</sub> ∽SiMe <sub>3 +</sub>		nitiator atalytic)	OSiMe <sub>3</sub>
1;	a (1.2 equiv) 2a (0	).10 mmol)	- N <sub>2</sub>	3aa
Entry	Initiator	mol%	Time	Yield [%] <sup>[a]</sup>
1	tBuOLi	10	1 h	91
2	Me₃SiOLi	10	1 h	> 95
3	Me₃SiONa	10	< 5 min	98 (70) <sup>[b]</sup>
4	Me₃SiOK	10	<5 min	90
5	Me₃SiONa	5	<5 min	> 95
6	Me₃SiONa	1	20 h	6
7	Me₃SiOK	1	20 h	58
8	CsF	10	20 h	60
9	TMAF	10	20 h	trace

[a] Determined by calibrated GLC analysis with tetracosane as an internal standard. [b] Yield of isolated product on a 0.40 mmol scale after flash chromatography on silica gel in parentheses. TMAF = tetramethylammonium fluoride.



slight excess of the diazene reagent 1a employed. In turn, compounds 4a and 5a were the major products of the alkoxide-initiated degradation of 1a in the absence of the aldehyde substrate (see the Supporting Information for details).

To demonstrate the scope of the new method, we continued with 10 mol % Me<sub>3</sub>SiONa in THF at room temperature as the standard procedure. Diazenes with silvl groups other than Me<sub>3</sub>Si were examined (**1b-d**; Table 2, entries 1–3). It was only the Me<sub>2</sub>PhSi-substituted derivative 1d that behaved similarly to 1a, affording the silvl ether 3da in 86% yield. Conversely, 1b, which has a Et<sub>3</sub>Si group, and 1c, which has a tBuMe<sub>2</sub>Si group, led to either low or no conversion of benzaldehyde. However, a little re-optimization showed that Me<sub>3</sub>SiOK instead of Me<sub>3</sub>SiONa promotes aryl transfer from 1b to benzaldehyde, and 3ba was isolated in 76% yield. The reaction of sterically more hindered 1c required the addition of 18-crown-6, and the "more naked" silanolate and alkoxide intermediate enabled the formation of the silyl ether 3ca in 68% yield. We also prepared a wide range of Me<sub>3</sub>Si-substituted diazenes with functionalized aryl groups (1e-o; Table 2, entries 4-14). Without exception, these reacted in good yields under the standard setup. The successful reaction of electron-rich 1 f to silvl ether 3 fa closes an important gap (cf. Scheme 1, top). Further notable examples include aryl transfers from diazenes 1g, 1h, and 1n, which contain sensitive functional groups (CO<sub>2</sub>Me in 3ga, CN in **3ha**, and NO<sub>2</sub> in **3na**). Even the transfer of aryl nucleophiles containing a bromo or iodo group, as in 1k and 11 (competing halogen-metal exchange), or a fluorine substituent in the ortho position, as in 1m (competing β-elimination/aryne formation), proceeded in high yields. These examples highlight the chemoselectivity of the method and its orthogonality with classical carbonyl arylations. The productive combination of these diazenes and a broad range of aromatic, heteroaromatic, and cinnamic aldehydes (2b-i) is

TUDIC 2	• Scope 1. •		Tuble 2. Scope 1. variation of the snyr and any groups of the diazene.									
FG	N: <sub>N</sub> -S		Me <sub>3</sub> SiONa (10 mol%)	FG	SiR <sub>3</sub>							
ĺ	N N		THF		$\square$							
<b>1b–o</b> (1.2 equiv) <b>2a</b> (0.40 mmol) – N <sub>2</sub> <b>3ba–oa</b>												
Entry	Diazene	SiR <sub>3</sub>	FG	Silyl ether	Yield [%]							
<b>]</b> <sup>[a]</sup>	1b	SiEt <sub>3</sub>	4-Me	3 ba	76							
2 <sup>[b]</sup>	lc	SitBuMe <sub>2</sub>	4-Me	3 ca	68							
3	1 d	$SiMe_2Ph$	4-Me	3 da	86							
4	le	SiMe <sub>3</sub>	Н	3 ea	72							
5	1 f	SiMe <sub>3</sub>	4-OMe	3 fa	82							
6 <sup>[a]</sup>	1g	SiMe <sub>3</sub>	4-CO <sub>2</sub> Me	3 ga	80							
7	1 h	SiMe <sub>3</sub>	4-CN	3 ha	72							
8	1i	SiMe <sub>3</sub>	4-F	3 ia	99							
9	1j	SiMe <sub>3</sub>	4-Cl	3 ja	81							
10	1 k	SiMe₃	4-Br	3 ka	87							
11	11	SiMe <sub>3</sub>	4-I	3 la	83							
12	1 m	SiMe <sub>3</sub>	2-F	3 ma	65							
13 <sup>[a]</sup>	ln	SiMe₃	3-NO <sub>2</sub>	3 na	67							
14	10	$SiMe_3$	2,5-Me <sub>2</sub> , 4-F	3 oa	73							

[a] Me<sub>3</sub>SiOK instead of Me<sub>3</sub>SiONa. [b] Me<sub>3</sub>SiOK/18-crown-6 (1.0:1.2 molar ratio) instead of Me<sub>3</sub>SiONa.

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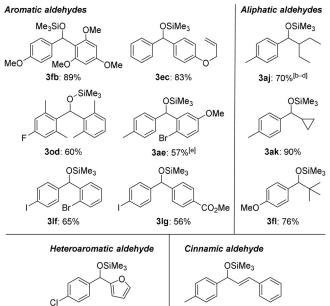


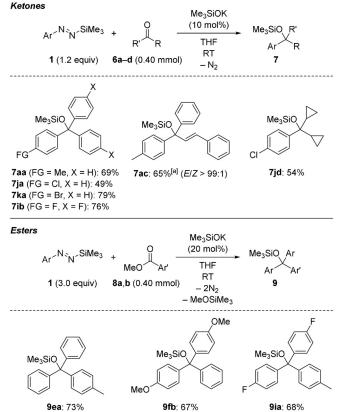
Figure 1. Scope II: Various diazene/aldehyde combinations.<sup>[a]</sup> [a] Unless noted otherwise, the reactions were performed on a 0.40 mmol scale with 10 mol % Me<sub>3</sub>SiONa in THF at room temperature. [b] Me<sub>3</sub>SiOK instead of Me<sub>3</sub>SiONa. [c] Formed along with the corresponding silyl enol ether in 30% yield. [d] Yield determined by NMR spectroscopy using  $CH_2Br_2$  as an internal standard. [e] The reaction was performed on a 1.8 mmol scale with 5.0 mol% Me<sub>3</sub>SiONa in THF at room temperature.

3ai: 73% (E/Z > 99:1)

3ih: 73%

further evidence of this (Figure 1). Enolizable aldehydes were not compatible but  $\alpha$ -branched 2-ethylbutyraldehyde (2j) yielded the silvl ether **3aj** in 70% yield along with the silvl enol ether in 30% yield. Other aliphatic aldehydes 2k and 2l reacted with high chemoselectivity to furnish 3ak and 3fl in good yields (Figure 1).

Less electrophilic ketones were also competent substrates but, as in the case of enolizable acetophenone, deprotonation was the predominant pathway to afford the corresponding silyl enol ether in 60% yield (not shown, see the Supporting Information). Conversely, **6a-d** reacted in the planned way with Me<sub>3</sub>SiOK as the initiator (Scheme 2, top). No reaction or low conversion were observed with Me<sub>3</sub>SiOLi and Me<sub>3</sub>SiONa, presumably because of the low reactivity of the intermediate tertiary alkoxide, and hence its inability to maintain catalytic turnover. Unlike the 1,2-selective aryl transfer to *trans*-cinnamaldehyde  $(2i \rightarrow 3ai, Figure 1)$ , the reaction of the aryl nucleophile with *trans*-chalcone (6c) led to the formation of both the 1,2-adduct (7ac, 65%) and the 1,4-adduct (6%). Moreover, modification of the reaction setup with a higher loading of Me<sub>3</sub>SiOK (20 mol%) and slow addition of the diazene (3 equiv) to a solution of a methyl benzoates 8 and THF even enabled two-fold aryl transfer to give the tertiary silvl ethers 9 in reasonable yields (Scheme 2, bottom). To the best of our knowledge, this is an unprecedented catalytic arylation of unactivated carboxylic acid derivatives with non-stabilized carbanion equivalents.<sup>[13]</sup> We note here that the occurrence of this nucleophilic addition is



Scheme 2. Scope III: Ketones and esters as electrophiles. [a] Formed along with the corresponding 1,4-adduct in 6% yield.

9ia: 68%

9ea: 73%

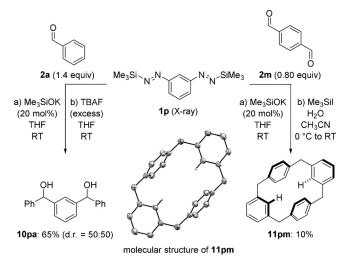
also diagnostic of the in situ formation of highly reactive aryl anions.[14]

Our next plan was to explore whether the diazene platform would also enable reactions of aryl dinucleophiles.<sup>[15]</sup> For this, we synthesized the 1,3-bismetalated benzene equivalent 1p from 1,3-diaminobenzene in 26% yield over three steps (see the Supporting Information for details and crystallographic characterization<sup>[16]</sup>). The bisdiazene **1p** is a storable deep-blue crystalline solid with decent thermal stability (up to 130 °C). The reaction of 1p and benzaldehyde (2a, 1.4 equiv) in the presence of 20 mol% Me<sub>3</sub>SiOK afforded diol 10pa in 65% yield after deprotection with TBAF (Scheme 3, left).

The fact that 10pa had been employed as a precursor of porphinoid macrocycles<sup>[17]</sup> inspired us to make use of building block 1p in the practical assembly of otherwise difficult-toprepare macrocycles. The idea was to combine 1,3-difunctional **1p** and terephthalaldehyde (**2m**) with its 1,4-substitution pattern, hoping that the alternate 1,3/1,4 motifs of the rings would result in cyclization rather than polymerization to poly(diarylcarbinols). The reaction of 1p and 0.80 equiv 2m initiated with 20 mol % Me<sub>3</sub>SiOK led to a complex product mixture of polymeric and oligomeric material, from which a tetrameric macrocyclic compound could be identified by HRMS analysis.<sup>[18]</sup> Defunctionalization of the crude residue, that is removal of the silyl ethers by a reported procedure,<sup>[19]</sup> considerably simplified the analysis and allowed the isolation of the unknown cyclophane-like [4]arene macrocycle 11 pm in

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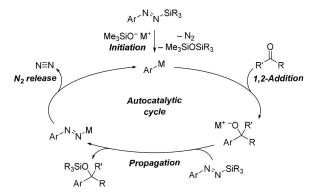




**Scheme 3.** Scope IV: Equivalent of an aryl bisnucleophile in the reaction with an aldehyde (left) or a dialdehyde (right); molecular structure of a cyclophane-like [4]arene macrocycle (middle, thermal ellipsoids are shown at the 50% probability level and all hydrogen atoms except the two pointing toward the center are omitted for clarity).

10% yield over two steps (Scheme 3, right).<sup>[20]</sup> This seemingly low yield compares well with others from difficult macrocyclizations involving aromatic precursors lacking preorganization, especially in relatively high concentration (0.1m).<sup>[21]</sup> The molecular structure of **11pm** was confirmed by X-ray diffraction<sup>[16]</sup> (Scheme 3, middle) and shows a preference for a chair-like conformation in the solid state, whereas a boatlike conformation was computed to be more stable by approximately 0.5 kcal mol<sup>-1</sup> (see the Supporting Information for details). Compound **11pm** is the simplest unfunctionalized member of an emerging class of hybrid macrocycles<sup>[22]</sup> that currently comprises just two derivatives.<sup>[23]</sup>

Although an in-depth mechanistic analysis is still pending, we propose the autocatalytic cycle outlined in Scheme 4. After initiation with either of the three trimethylsilanolate alkali salts, the aryl alkali metal will form as a result of desilylation and loss of  $N_2$ . The in situ formed aryl nucleophile then adds to the carbonyl compound, forming an alkali metal alkoxide that will in turn engage in the desired degradation of



**Scheme 4.** Proposed autocatalytic cycle. M = alkali metal, R and R' = alkyl or aryl, Ar = aryl.

the diazene reagent. This step then propagates the catalytic cycle.

To summarize, we have shown that N-aryl-N'-silyldiazenes constitute a versatile platform from which various highly reactive and, at the same time, functionalized aryl nucleophiles can be released at ambient temperature. The reaction of a related bisdiazene illustrates the potential of the method to formally generate dinucleophiles. These reactive intermediates can be trapped in situ with functionalized carbonyl and carboxyl compounds. Conceptually, these arylation reactions are similar to a Barbier-like setup,<sup>[24]</sup> where the polar organometallics are generated in situ, thereby avoiding their delicate preparation and handling. However, our method makes use of  $Me_3SiOM$  (with M = Li, Na, and K)<sup>[11]</sup> species as initiators, whereas Barbier reactions typically rely on overstoichiometric amounts of reducing metals. Aside from its excellent functional-group tolerance, this new method differs from established ones in that it is halidefree, starting from aryl hydrazines rather than aryl halides.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:**  $autocatalysis \cdot chemoselectivity \cdot Lewis bases \cdot nucleophilic addition <math>\cdot$  silicon

- Organometallics in Synthesis: Third Manual (Ed.: M. Schlosser), Wiley, Hoboken, 2013.
- [2] a) A. D. Benischke, M. Ellwart, M. R. Becker, P. Knochel, Synthesis 2016, 48, 1101–1107; b) G. Dagousset, C. François, T. León, R. Blanc, E. Sansiaume-Dagousset, P. Knochel, Synthesis 2014, 46, 3133–3171; c) P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis, V. A. Vu, Angew. Chem. Int. Ed. 2003, 42, 4302–4320; Angew. Chem. 2003, 115, 4438–4456.
- [3] W. E. Parham, C. K. Bradsher, Acc. Chem. Res. 1982, 15, 300-305.
- [4] Yoshida and co-workers introduced flow technology as an alternative to batch reactions: a) A. Nagaki, *Tetrahedron Lett.* 2019, 60, 150923; b) A. Nagaki, J.-i. Yoshida, *Top. Organomet. Chem.* 2016, 57, 137–175.
- [5] H. J. Reich in *Lewis Base Catalysis in Organic Synthesis* (Eds.: E. Vedejs, S. E. Denmark), Wiley-VCH, Weinheim, **2016**, pp. 233–280.
- [6] a) N. Ishikawa, K.-i. Isobe, Chem. Lett. 1972, 435-436; b) F. Effenberger, W. Spiegler, Angew. Chem. Int. Ed. Engl. 1981, 20, 265-266; Angew. Chem. 1981, 93, 287-288; c) F. Effenberger, W. Spiegler, Chem. Ber. 1985, 118, 3872-3899; d) F. Effenberger, W. Spiegler, Chem. Ber. 1985, 118, 3900-3914; e) M. Ueno, C. Hori, K. Suzawa, M. Ebisawa, Y. Kondo, Eur. J. Org. Chem. 2005, 1965-1968; f) K. Suzawa, M. Ueno, A. E. H. Wheatley, Y.

12340 www.angewandte.org © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim Angew. Chem. Int. Ed. 2020, 59, 12337–12341



Kondo, *Chem. Commun.* **2006**, 4850–4852; g) M. Das, D. F. O'Shea, *J. Org. Chem.* **2014**, *79*, 5595–5607.

- [7] A. S. Pilcher, P. DeShong, J. Org. Chem. 1996, 61, 6901-6905.
- [8] R. Lerebours, C. Wolf, J. Am. Chem. Soc. 2006, 128, 13052– 13053.
- [9] C. Chauvier, L. Finck, S. Hecht, M. Oestreich, *Organometallics* 2019, 38, 4679-4686.
- [10] J. C. Bottaro, J. Chem. Soc. Chem. Commun. 1978, 990.
- [11] For a review of trimethylsilanolate alkali salts, see: K. Bürglová, J. Haláč, Synthesis 2018, 50, 1199–1208.
- [12] A. R. Katritzky, J. Wu, S. V. Verin, Synthesis 1995, 651-653.
- [13] For the addition of stabilized heteroaryl anions to lactones, see: A. Ricci, M. Fiorenza, M. A. Grifagni, G. Bartolini, *Tetrahedron Lett.* 1982, 23, 5079-5082.
- [14] 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, 5178–5183; *Angew. Chem.* 2007, 119, 5270–5275.
- [15] a) M. Fossatelli, R. den Besten, H. D. Verkruijsse, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 527–528; b) F. Bickelhaupt, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 990–1005; *Angew. Chem.* **1987**, *99*, 1020–1035.
- [16] CCDC 1971069 (1p) and 1971057 (11pm) contain the supplementary crystallographic data for this paper. These data can be obained free of charge from The Cambridge Crystallographic Data Centre.
- [17] M. Stępień, L. Latos-Grażyński, Chem. Eur. J. 2001, 7, 5113– 5117.

- [18] Larger macrocycles such as the [6]arene derivative were also observed by HRMS but could not be isolated nor characterized after defunctionalization.
- [19] E. J. Stoner, D. A. Cothron, M. K. Balmer, B. A. Roden, *Tetrahedron* 1995, 51, 11043-11062.
- [20] For the synthesis of parent [1,1,1,1]metacyclophane, see: a) J. E. McMurry, J. C. Phelan, *Tetrahedron Lett.* **1991**, *32*, 5655–5658; for the synthesis of parent [1,1,1,1]paracyclophane, see: b) Y. Miyahara, T. Inazu, T. Yoshino, *Tetrahedron Lett.* **1983**, *24*, 5277–5280.
- [21] Examples are provided in the following review: V. Martí-Centelles, M. D. Pandey, M. I. Burguete, S. V. Luis, *Chem. Rev.* 2015, 115, 8736-8834.
- [22] An example of an application of a hybrid macrocycle: D. A. Fowler, A. S. Rathnayake, S. Kennedy, H. Kumari, C. M. Beavers, S. J. Teat, J. L. Atwood, J. Am. Chem. Soc. 2013, 135, 12184–12187.
- [23] a) T. Boinski, A. Cieszkowski, B. Rosa, A. Szumna, J. Org. Chem. 2015, 80, 3488-3495; for a brief discussion of so-called hybrid[n]arenes, see: b) J.-R. Wu, Y.-W. Yang, Chem. Commun. 2019, 55, 1533-1534.
- [24] P. Barbier, C. R. Chim. 1899, 128, 110.

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