Heterocoupling of Different Aryl Nitrenes to Produce Asymmetric Azoarenes Using Iron-Alkoxide Catalysis and Investigation of the *Cis-Trans* Isomerism of Selected Bulky Asymmetric Azoarenes

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Abstract

Heterocoupling of different aryl nitrenes (originating in organoazides) to produce asymmetric azoarenes using two different iron-alkoxide catalysts is reported. $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ was previously shown to catalyze homocoupling of a variety of aryl nitrenes. While bulky nitrenes featuring *ortho* substituents were coupled more efficiently, coupling of the less bulky *meta*- and *para*-substituted aryl nitrenes was also demonstrated. In contrast, iron(II) complex of a chelating bis(alkoxide) ligand, $Fe[OO]^{Ph}(THF)_2$, was previously shown to couple efficiently non-bulky aryl nitrenes lacking substituents in *ortho* positions. In the present work, we demonstrate that the combination of two different nitrenes (10 equivalents overall, 5 equivalents each) with $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ (10 mol%) produced statistical, or close to statistical distribution (25:25:50 for the two homocoupled products and the heterocoupled product, respectively) for various combinations containing one or two *ortho* alkyl substituents at one nitrene and a single *ortho* alkyl group at another. Surprisingly, the combination of $Fe[OO]^{Ph}(THF)_2$ with two different non-bulky organoazides was found to catalyze primarily homocoupling of the resulting aryl nitrenes (21-49%), with a smaller proportion (~8-15%) of the asymmetric product forming. Six different heterocoupled products featuring one or two alkyl groups in the *ortho* positions were isolated as a mixture of *cis* and *trans* isomers at room temperature, and characterized by NMR spectroscopy, UV-vis spectroscopy, and HRMS. Following their isolation, *cis*-*trans* isomerism in these species was investigated. Heating the *cis*-*trans* mixture to 60 °C produced *trans* isomer cleanly, while shining UV light on the *cis*-*trans* mixture significantly increased the amount of the *cis* isomer (up to 90%). The *cis* isomer was found to be relatively stable, exhibiting $t_{1/2}$ values of approximately 10 days at room temperature.

Introduction

Azoarenes ArN=NAr are important compounds that found large-scale applications in the chemical industry as dyes and indicators.[1,2] Many additional potential applications of azoarenes are currently being investigated, including molecular switches, sensors, molecular shuttles, and others.[3-9] Azoarenes have been also demonstrated to serve as the imido group precursors in the early transition metal mediated synthesis of pyrroles and carbodiimides.[10-12] Azoarenes are commonly produced by the azo coupling reaction, or by other stoichiometric routes that are prone to generating stoichiometric amounts of potentially toxic by-products.[1] Therefore, there is a significant interest in the development of more sustainable routes towards azoarenes. Several groups have recently reported catalytic synthesis of symmetric azoarenes from organoazides using transition metal catalysis.[13-22] In general, this synthetic route uses environmentally friendly base metal catalysts, avoids using toxic co-reactants, and produces only N_2 as a by-product. The reaction proceeds via a transition metal mediated formation of aryl nitrenes, which subsequently undergo homocoupling. However, most industrially viable azoarenes are asymmetric, bearing two different aryl groups. While the stoichiometric synthesis of heterocoupled azoarene via the reaction of metal-nitrene with a different azide precursor has been reported,[21] it is less clear whether asymmetric (heterocoupled) azoarenes can be produced catalytically from a mixture of two different organoazides. Herein, we demonstrate a rare example of transition-metal-catalyzed heterocoupling of aryl nitrenes.

As part of our broader investigation of the group transfer reactivity of base transition metal alkoxide complexes,[23-27] we have previously reported three different iron-alkoxide pre-catalysts of the $Fe(OR)_2(THF)_2$ general form that displayed markedly different reactivity in nitrene homocoupling (**Figure 1**).[18-20] The first generation pre-catalyst $Fe(OC^tBu_2Ph)_2(THF)_2$ (**1**)

was able to carry out highly efficient homocoupling of mesityl nitrene to produce azomesitylene.[18] However, its reactivity was limited to bulky aryl azides only; the reaction with less bulky aryl azides (lacking two *ortho* substituents) produced μ-imido complexes that failed to demonstrate nitrene coupling. The limited reactivity scope of **1** was ascribed to the relative instability of the bis(alkoxide) ligation for [OC^{t}Bu$_2$Ph], as the formation of the decomposition product Fe(OC^{t}Bu$_2$Ph)$_3$ was observed over time.[18] Our second generation catalyst, featuring bulkier alkoxide ligand, Fe(OC^{t}Bu$_2$(3,5-Ph$_2$C$_6$H$_3$))$_2$(THF)$_2$ (**2**), exhibited more stable bis(alkoxide) ligation.[19] As a result, it demonstrated more robust nitrene homocoupling reactivity for a broader range of substrates (**Figure 1**).[19] Although the reaction with *ortho*-substituted nitrenes was the most efficient (nearly quantitative yields), this catalyst was also able to conduct homocoupling of less bulky *meta*-substituted and even *para*-substituted aryl nitrenes (generally at 60 °C), with yields between 30-70%. Computational and spectroscopic mechanistic studies suggested that azoarene formation proceeded via the initial formation of the metal-nitrene intermediate, followed by its dimerization to form azoarene (**Figure 2**).[19] The need for the thermal conditions can be traced back to the formation of dark-green tetrazene by-products, which had to be transformed back into the reactive metal-nitrene for the catalytic reaction to take place. Following these results, we became interested in the heterocoupling reactivity of this catalyst, using 1:1 combination of various aryl azides. We have also reported the synthesis and reactivity of an iron complex with a chelating bis(alkoxide) ligand, Fe[OO]^{Ph}(THF)$_2$ (**3**), that selectively coupled non-bulky aryl nitrenes (with *meta*/*para* substituents); no reactivity was observed for mesityl and related di-*ortho*-substituted aryl azides.[20] Herein we describe the heterocoupling reactivity of both complexes **2** and **3**. Several new asymmetric azoarenes were isolated and their *cis*:*trans* isomerization was studied.

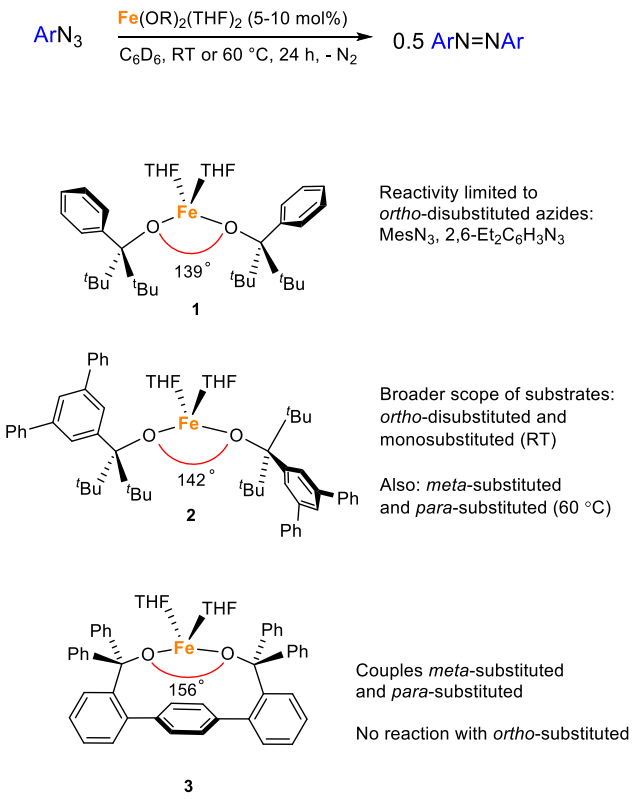


Figure 1. Nitrene homocoupling reactivity of the family of iron bis(alkoxide) complexes.

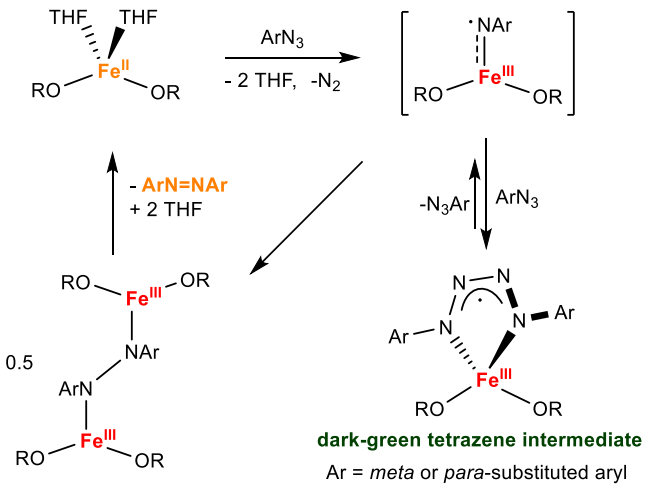


Figure 2. Mechanism of nitrene coupling mediated by **2** (OR = $OC^tBu_2(3,5\text{-}Ph_2C_6H_3)$).

Results and Discussion

Heterocoupling reactivity of $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ (2)

As described in the introduction, $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ (**2**) exhibited the broadest substrate scope, which included both bulky and non-bulky aryl azides.[19] Thus, our initial study focused on the heterocoupling reactivity of **2**. The reactivity of **2** (10 mol%) was investigated using 10 equivalents overall (5 equivalents each) of two different substituted aryl azides (**Scheme 1**), and the results are presented in **Table 1**. Specifically, we have investigated a combination of two bulky *ortho*-disubstituted aryl azides ($MesN_3$ and $2,6\text{-}Et_2C_6H_3N_3$, entry 1), a combination of a bulky *ortho*-disubstituted aryl azide ($MesN_3$ or $2,6\text{-}Et_2C_6H_3N_3$) with less bulky *ortho*-monosubstituted aryl azides ($2\text{-}MeC_6H_3N_3$, $2\text{-}EtC_6H_3N_3$, and $2\text{-}^iPrC_6H_3N_3$, entries 2-6), a combination of two *ortho*-monosubstituted aryl azides ($2\text{-}EtC_6H_3N_3$ and $2\text{-}^iPrC_6H_3N_3$, entry 7), a combination of bulky ($MesN_3$) azide and non-bulky ($3,5\text{-}Me_2C_6H_3N_3$) azide (entry 9) and a combination of two non-bulky azides ($3,5\text{-}Me_2C_6H_3N_3$ and $4\text{-}MeC_6H_4N_3$, entry 8). We have also explored the combination of $MesN_3$ and $3,5\text{-}Me_2C_6H_3N_3$ with three different halo-substituted aryl azides (entries 10-12). A simple statistical product distribution for the combination of Ar^1N_3 and Ar^2N_3 would entail the formation of Ar^1NNAr^1:Ar^1NNAr^2:Ar^2NNAr^2 in a 25:50:25 ratio. Different overall yields and product distributions were observed for the different combinations of aryl azides. The combination of two *ortho*-disubstituted or *ortho*-disubstituted with *ortho*-monosubstituted azides result in the overall quantitative conversion of aryl azides into the corresponding azoarenes. The combination of *ortho*-disubstituted aryl azide with *ortho*-monosubstituted aryl azide follows the approximately statistical distribution (entries 2-4 and 6, **Table 1**). In contrast, the combination of two *ortho*-disubstituted azides, mesityl azide with 2,6-diethylphenyl azide, produced larger (40%) portions of the respective homocoupled product and

smaller (20%) portion of the heterocoupled product (entry 1, **Table 1**). A combination of 2,6-diethylphenyl azide and 2-methylphenyl azide led to the formation of approximately 33% of each product (entry 5, **Table 1**). The combination of *ortho*-monosubstituted azides (2-ethylphenyl azide and 2-^{i}propylphenyl) produced a nearly statistical distribution of the products (16% of each homocoupled azoarene and 30% of the heterocoupled azoarene product), albeit in somewhat lower overall yield (entry 7, **Table 1**).

Scheme 1. Heterocoupling reactivity studies.

Table 1. Heterocoupling reactivity of Fe(OC^{t}Bu$_2$(3,5-Ph$_2$C$_6$H$_3$))$_2$(THF)$_2$ (**2**). The reaction was conducted as described in **Scheme 1** above.

Entry	**Ar^{1}N$_3$**	**Ar^{2}N$_3$**	**Ar^{1}NNAr^1** (%)	**Ar^{2}NNAr^2** (%)	**Ar^{1}NNAr^2** (%)	**Ar^{1}N$_3$** (%)	**Ar^{2}N$_3$** (%)
1	MesN$_3$	2,6-Et$_2$C$_6$H$_3$N$_3$	40	40	20	-	-
2	MesN$_3$	2-CH$_3$C$_6$H$_4$N$_3$	25	25	50	-	-
3	MesN$_3$	2-EtC$_6$H$_4$N$_3$	25	25	50	-	-
4	MesN$_3$	2-^{i}PrC$_6$H$_4$N$_3$	20	20	60	-	-
5	2,6-Et$_2$C$_6$H$_3$N$_3$	2-CH$_3$C$_6$H$_4$N$_3$	33	33	33	-	-
6	2,6-Et$_2$C$_6$H$_3$N$_3$	2-^{i}PrC$_6$H$_4$N$_3$	25	25	50	-	-
7	2-EtC$_6$H$_4$N$_3$	2-^{i}PrC$_6$H$_4$N$_3$	16	16	30	15	18
8	3,5-Me$_2$C$_6$H$_3$N$_3$	4-CH$_3$C$_6$H$_4$N$_3$	11	13	12	33	31
9	MesN$_3$	3,5-Me$_2$C$_6$H$_3$N$_3$	2	40	10	38	0
10	MesN$_3$	2-ClC$_6$H$_4$N$_3$	2	31	2	47	16
11	MesN$_3$	2,6-Br$_2$C$_6$H$_3$N$_3$	3	39	2	46	10
12	3,5-Me$_2$C$_6$H$_3$N$_3$	3,5-Cl$_2$C$_6$H$_3$N$_3$	8	10	11	29	0

The combination involving non-bulky (*meta*/*para*-substituted) aryl azides (entries 8 and 9) generally displayed lower overall yields, with significant amounts of azides remaining. We have previously demonstrated that the reaction of **2** with non-bulky aryl azides (lacking *ortho* substituents) led initially to the formation of dark-green tetrazene complexes $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3)_2(ArNNNNAr)$ (see **Figure 2**), which were characterized by X-ray crystallography, Mössbauer spectroscopy, and EPR.[19] Similarly, a combination of *meta*- and *para*-substituted azides (3,5-dimethylphenyl azide and 4-methylphenyl azide) in the present case exhibited a characteristic reaction color change from light brown to dark green, suggesting tetrazene formation. The reaction displayed overall lower reactivity, producing 11% and 13% homocoupled products, and 12% of the heterocoupled product (entry 8, **Table 1**). Surprisingly, the reaction between mesityl azide and 3,5-dimethylphenyl azides showed much higher yields of homocoupled product of 3,5-dimethylphenyl azide (40%) (entry 9, **Table 1**). The reaction color change to dark-green suggested again the formation of the stable tetrazene complex with 3,5-dimethylphenyl azide ($Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3)_2((3,5\text{-}Me_2C_6H_3)NNNN(3,5\text{-}Me_2C_6H_3))$), which was previously isolated and spectroscopically characterized.[19] The introduction of the electron-deficient substituents (entries 10-12) does not lead to a significant difference in the reaction outcome. For the combinations of (bulky) $MesN_3$ with $2\text{-}ClC_6H_4N_3$ or $2,6\text{-}Br_2C_6H_3N_3$, mostly the homocoupling of the less bulky nitrene is observed. The combination of two non-bulky azides $3,5\text{-}Me_2C_6H_3N_3$ and $3,5\text{-}Cl_2C_6H_3N_3$ (entry 12) results in comparable amounts of all possible products, similar to the reaction of $3,5\text{-}Me_2C_6H_3N_3$ and $4\text{-}MeC_6H_4N_3$ (entry 8).

The catalytic nitrene heterocoupling reactivity by complex **2** can be rationalized using the previously described nitrene coupling mechanism (**Figure 2**), with the steric effect at the metal-nitrene functionality being primarily responsible for the reaction outcome. Bulky metal-nitrene

intermediates are more reactive, less likely to form tetrazenes, and undergo overall efficient and generally statistical coupling (with the exception of $MesN_3$+2,6-$Et_2C_6H_3N_3$, entry 1). In contrast, the combination of the bulky and the non-bulky electron-rich aryl azides demonstrates mostly the homocoupling of the non-bulky aryl nitrene, with little participation of the generally more reactive bulkier counterpart. This is likely due to the facile formation of the tetrazene species with the non-bulky aryl azides.[19] As the catalyst is in the form of tetrazene species (**Figure 2**), it is unavailable to react with $MesN_3$. Aryl azides bearing one or two halo substituents in the *ortho* positions (entries 10 and 11) exhibit reactivity pattern more akin to the non-bulky aryl azides (entry 8) than bulky aryl azides (entries 1-7). This difference in the reactivity between methyl and halo substituents in *ortho* positions can be traced back to their significant steric differences predicted by the corresponding A-values (Me, 1.7 vs. ~0.4 for Br and Cl).[28] It also supports the notion that the steric bulk of aryl azide is primarily responsible for its reactivity. The results above suggest that to produce the heterocoupled product in a high (approximately statistical) yield, both aryl azides need to be bulky, with one of the aryl azide featuring two substituents in *ortho* position, and the other being mono-substituted. The heterocoupled products obtained in relatively high yields (entries 1-6) were isolated and their properties were investigated (see below).

Heterocoupling reactivity of $Fe[OO]^{Ph}(THF)_2$ (3)

We have also explored the heterocoupling reactivity involving $Fe[OO]^{Ph}(THF)_2$ (complex **3**). Complex **3** exhibited selectivity for the homocoupling of non-bulky aryl azides.[20] Thus, *p*-tolyl, *p*-chlorophenyl/bromophenyl, *p*-trifluoromethylphenyl, and *m*-dimethylphenyl azides produced the corresponding symmetric azoarenes in moderate to high yields (64-85%). The heterocoupling reactivity of **3** was studied similarly to the reactivity of **2** (**Scheme 1**), using 10

equivalents overall (5 each) of two different aryl azides with 10 mol% of the catalyst. The catalysis products were identified by ^{1}H NMR and GC-MS, and the results are presented in **Table 2**. As *p*-tolyl azide was among the most efficient substrates for **3**, we have investigated its combination with *p*-halophenyl (entry 1 and 2), *p*-trifluoromethylphenyl (entry 3), *m*-dimethylphenyl (entry 4), and *m*-trifluoromethylphenyl (entry 5). In addition, the combination of *p*-tolyl azide with mesityl azide was investigated (entry 6). Surprisingly, and in a sharp contrast to the reactivity exhibited by complex **2**, complex **3** preferentially catalyzes the formation of the symmetric products. The symmetric azoarenes form in the overall similar quantities (~30-40% yield), while the asymmetric azoarene generally forms in ~10% yield. The combination of *p*-tolyl azide with mesityl azide constitutes a notable exception to this pattern (entry 6), as only one of the substrates (*p*-tolyl) forms the corresponding symmetric azoarene, and the formation of the asymmetric product is negligible. This behavior is not unanticipated, as catalyst **3** has previously demonstrated the lack of reactivity with mesityl azide.

Table 2. Heterocoupling reactivity of $Fe[OO]^{Ph}(THF)_2$ (**3**). The reaction was conducted as described in **Scheme 1** above.

Entry	**Ar^1N_3**	**Ar^2N_3**	**Ar^1NNAr^1** (%)	**Ar^2NNAr^2** (%)	**Ar^1NNAr^2** (%)	**Ar^1N_3** (%)	**Ar^2N_3** (%)
1	4-$CH_3C_6H_4N_3$	4-$ClC_6H_4N_3$	26	21	12	10	11
2	4-$CH_3C_6H_4N_3$	4-$BrC_6H_4N_3$	21	26	11	11	10
3	4-$CH_3C_6H_4N_3$	4-$CF_3C_6H_4N_3$	27	40	14	10	0
4	4-$CH_3C_6H_4N_3$	3,5-$Me_2C_6H_3N_3$	38	34	15	7	0
5	4-$CH_3C_6H_4N_3$	3-$CF_3C_6H_4N_3$	24	49	8	10	0
6	4-$CH_3C_6H_4N_3$	$MesN_3$	19	0	4	3	36

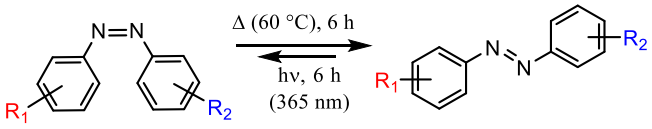
C*is-trans* isomerism in asymmetric azoarenes featuring alkyl substitution

Light-sensitive *cis*-*trans* isomerization is one of the most important properties of azoarenes. Due to this property, azoarenes are used as molecular photoswitches and drug delivery agents.[1-9] A very significant amount of work was conducted on the factors influencing *cis*-*trans* isomerism in various symmetric and asymmetric azoarenes.[29,30] Generally, *trans*-isomer of an azoarene is more stable and the relative stability of the *cis* isomer is affected by the overall substitution pattern of the azoarene. The stability of the *cis*-isomer of an azoarene was reported to increase with symmetric tetra-*ortho* aryl substitution of heteroatoms (OR, SR, NR_2, Cl, F).[31-35] Similarly, asymmetric arylazopyrazoles[36,37] were reported to exhibit higher stability of the *cis* (*Z*) form with increasing *ortho* substitution of the aryl and pyrazoles.[38-42] Symmetric azoarenes featuring alkyl groups in the *ortho* positions (i.e. Mes, 2,6-$Et_2C_6H_3$) are generally isolated cleanly as a *trans* isomer only, likely due to the steric hindrance from both sides.[18,19,21] However, relatively little is known about *cis*-*trans* isomerism of asymmetric azoarenes bearing different alkyl substitution in the *ortho* positions of the two aryls. One could postulate that a different substitution pattern of the aryls, particularly if only one of the *ortho* groups is present at one of the aryl rings, could benefit the stability of the *cis* isomer. Complex **2** enables efficient access to such species, allowing us to study their properties. To shed light on the *cis*-*trans* isomerism of the asymmetric azoarenes featuring bulky aryl groups, we have isolated heterocoupled products which were obtained in approximately statistical yields (**Table 3**). Azoarenes MesN=N(2-$^{i}PrC_6H_4$) (**4**), MesN=N(2-MeC_6H_4) (**5**), MesN=N(2-EtC_6H_4) (**6**), (2,6-$Et_2C_6H_3$)N=N(2-$^{i}PrC_6H_4Ph$) (**7**), (2,6-$Et_2C_6H_3$)N=N(2-MeC_6H_4) (**8**), and MesN=N(2,6-$Et_2C_6H_3$) (**9**) were purified by column chromatography and isolated in 43%, 36%, 34%, 37%, 25% and 16% overall yields, respectively. While these yields are relatively low, they reflect the statistical distribution of the

observed products, in which NMR yields of the heterocoupled products were ~50%. ^{1}H NMR spectroscopy (C_6D_6) revealed the presence of both *cis* and *trans* isomers at room temperature. While the *trans* isomer was dominant (69-86%, see **Table 3**), significant amounts of *cis* isomers (14-31%) were also observed.

Table 3. *Cis-trans* isomerization of isolated heterocoupled azoarenes.

Heterocoupled Azoarene	**#**	**As isolated by chromatography**		**Heating for 2 h (60 ^{0}C)**		**Irradiation for 2 h (365 nm)**		**Irradiation for 6 h (365nm)**	
		Trans (%)	*Cis* (%)	*Trans* (%)	*Cis* (%)	*Trans* (%)	*Cis* (%)	*Trans* (%)	*Cis* (%)
MesN=N(2-^{i}PrC$_6$H$_4$)	**4**	75	25	100	0	60	40	11	89
MesN=N(2-MeC$_6$H$_4$)	**5**	81	19	100	0	59	41	10	90
MesN=N(2-EtC$_6$H$_4$)	**6**	86	14	100	0	66	34	10	90
(2,6-Et$_2$C$_6$H$_3$)N=N(2-^{i}PrC$_6$H$_4$)	**7**	69	31	100	0	59	41	16	84
(2,6-Et$_2$C$_6$H$_3$)N=N(2-MeC$_6$H$_4$)	**8**	74	26	100	0	69	31	25	75
MesN=N(2,6-Et$_2$C$_6$H$_3$)	**9**	80	20	100	0	67	33	33	67



Scheme 2. *Cis-trans* isomerization observed for azoarenes **4-9**.

Relative stability of *cis* and *trans* isomers was studied at higher temperature and/or under irradiation (**Scheme 2**). Heating all azoarenes to 60 °C for 2 h results in a complete conversion of the mixture to the *trans* form. Pure *trans* products were characterized by ^{1}H and ^{13}C NMR spectroscopy at 60 °C. Thus, **Figure 3** demonstrates that while MesN=N(2-^{i}PrC$_6$H$_4$) is obtained in a 75:25 *trans*:*cis* ratio at room temperature, heating to 60 °C produces clean spectrum of the *trans* product only. In contrast, exposure of the samples to the UV light (365 nm) for 2 hours increases significantly the amount of the *cis* isomer in the sample. Further exposure (for 6 h)

makes the *cis* isomer predominant in the mixture, although the exact ratio depends on the azoarene. As **Figure 3** demonstrates, only traces of the *trans* product (<10%) are observed for MesN=N(2-^{i}PrC$_6$H$_4$) (**4**) after the irradiation for 6 h. A similar trend was observed for all other isolated asymmetric azoarenes after exposure to the UV light (**Table 3**). Longer irradiation (12 h) did not lead to significantly different results.

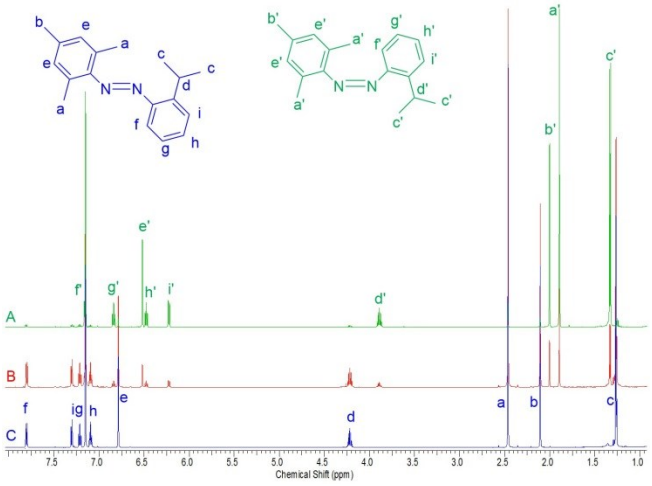


Figure 3. Spectrum of MesN=N(2-^{i}PrC$_6$H$_4$) (**4**): **A** = after exposure to UV (365 nm) light for 6 hours, **B** = as isolated, **C** = after heating for 2 h at 60 ºC.

Compounds **4-9** exhibit similar UV-vis spectra of the *cis-trans* mixtures. We have collected UV-vis spectra for the pure *trans* and predominantly *cis* forms for selected azoarenes (Figures S181-S194). The spectra of MesN=N(2-^{i}PrC$_6$H$_4$) (**4**) are presented in **Figure 4**. *Trans*-**4** exhibits n-π* band around 480 nm (responsible for its red-orange color), whereas *cis*-**4** exhibits the n-π* band around 460 nm (responsible for the compound's orange color). In comparison, the corresponding values for azobenzene are around 450 nm.[30] The π-π* band appears at 331 nm for the *trans*-**4** (320 nm for *trans*-azobenzene), and at 329 nm for *cis*-**4** (270 nm for azobenzene).

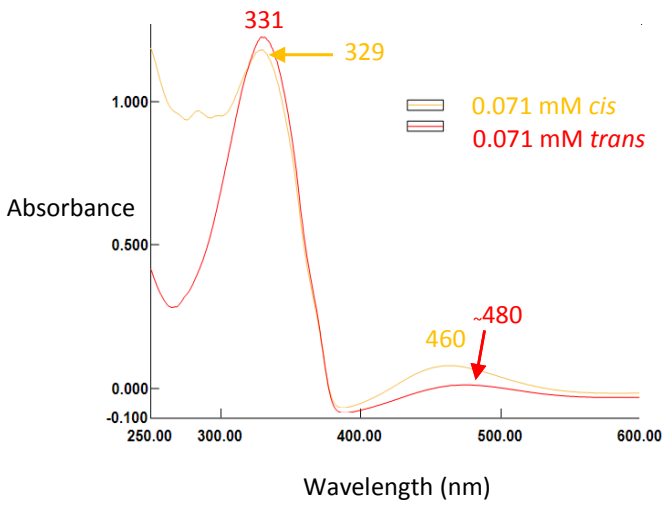


Figure 4. UV-vis spectra of *trans*-**4** and *cis*-**4**. The spectra were collected in hexane.

We have also studied the stability of the *cis* isomers at room temperature in benzene solution, by monitoring its ^{1}H NMR spectrum over time (Table S1). NMR demonstrates that after 10 days approximately 50% of **4** remains in the *cis* form. Similar $t_{1/2}$ values were observed for the other azoarenes. Although these values are relatively long compared with unsubstituted azoarenes, they are significantly shorter than the $t_{1/2}$ values for *ortho*-tetrafluoro azoarene (~700 days),[34] and are comparable with $t_{1/2}$ of the *ortho*-tetramethoxy derivative (~ 2 weeks).[31]

4.5. Summary and conclusions

$Fe(OC^{t}Bu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ (**2**) demonstrated a rare capability to catalyze heterocoupling reactivity for various combinations of bulky aryl azides. The specific combination of *ortho*-monosubstituted aryl azides with *ortho*-disubstituted aryl azides led to the production of the heterocoupled products in ~50% yields and thus the resulting products could be easily separated and characterized. In contrast, any combination involving less bulky *meta*/*para* substituted aryl azide did not lead to the production of the heterocoupled product in a good yield

due to the formation of stable tetrazene complexes $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(ArNNNNAr)$. Six new bulky asymmetric azoarenes featuring *ortho*-alkyl substitution were isolated and their *cis*-*trans* isomerism was investigated. All azoarenes demonstrated the presence of both isomers in solution at room temperature, with the *trans* isomer being the predominant one. Thermal conditions lead to the full conversion of the mixture to the *trans* isomer in all cases, while the irradiation of the mixture with the UV light (365 nm) leads to the predominant formation of the *cis* isomer, which decays relatively slowly to the *trans*/*cis* mixture. Overall, this work demonstrated the ability to catalytically produce asymmetric azoarenes which could be of potential interest as molecular switches or dyes from organoazides. As organoazides are among the most easily accessible functionalities in chemistry and biology, it potentially opens the way to the wider utilization of this simple heterocoupling method.

Experimental

General Methods and Procedures

Air-sensitive reactions were carried out in a nitrogen-filled glovebox. Benzene-d_6 (C_6D_6) was purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. HPLC grade non-deuterated solvents were purchased from Sigma-Aldrich and purified using an MBraun solvent purification system. Compounds were generally characterized by ^1H and ^{13}C NMR, and high-resolution mass spectrometry. Chemical shifts and coupling constants (*J*) were reported in parts per million and Hertz respectively. Thermofisher Scientific LTQ Orbittrap XL mass spectrometer at the Lumigen Instrument Center was used for high resolution mass spectra. GC-MS analysis was done using Agilent 6890N spectrometer, Thermo TG5MS 30m × 0.32mm × 0.25μm column, 7683 series injector, and Agilent 5973 detector. Irradiation of azoarenes (365

nm) was carried out using UVP® 95-0343-01 3UV™ Model 3UV-38 Handheld UV Lamp (8 W).

Caution! Organoazides are potentially explosive reagents that can be heat- or shock-sensitive, and should be handled with great care. The ratio of carbon to nitrogen atoms in a compound can serve as an approximate guideline to working with an organoazide. Organoazide with C/N ratios between 3 and 1 should generally be prepared exercising maximum caution, and should be stored only as dilute solutions (<1 M) in relatively small quantities. Organoazides with C/N ratios below 1 should never be isolated. The following references provide additional information regarding the appropriate handling of organoazides.[43-45]

General procedure for catalytic formation of azoarenes

$Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ (**2**) and $Fe[OO]^{Ph}(THF)_2$ (**3**) were synthesized as previously described.[19, 20] All azides were synthesized using previously reported procedures. Catalytic reactions were performed by adding 5 equivalents of each organic azide (10 equivalents overall) and 1,3,5-trimethoxy benzene (TMB) (or hexafluorobenzene (HFB)) as an internal standard solution in C_6D_6 to the C_6D_6 solution of the respective iron-alkoxide catalyst (10 mol%) in the N_2-filled glovebox. The reaction mixture was stirred at 60 ºC for 24 h. Yields of azoarenes were calculated by ^1H NMR; the spectra were compared to the previously published NMR spectra of the corresponding homocoupled azoarenes. Formation of all azoarenes was confirmed by GC-MS. Heterocoupled azoarenes which were obtained in ~50% yields were isolated in a pure state using silica gel column chromatography (hexane) and fully characterized by ^1H NMR, ^{13}C NMR, UV-vis, and HRMS. All isolated azoarenes (**4**-**9**) were obtained as mixtures of *cis* and *trans* isomers (^1H NMR spectroscopy). In all cases, the mixture can be fully

transformed to the *trans* isomer by heating to 60 °C for 2 h. Irradiation with UV light (365 nm) enables the formation of the predominantly *cis* isomer (up to 90%). Both *trans* and (predominantly) *cis* isomers were characterized by ^{1}H and ^{13}C NMR, and by UV-vis spectroscopy.

Synthesis and characterization of azoarenes 4-9

MesN=N(2-^{i}PrC$_6$H$_4$) (4). The reaction was carried out according to the general procedure by reacting 30.0 mg (0.032 mmol) of **2** with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 25.8 mg (0.159 mmol, 5 equiv) of 2-isopropylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene **4** was isolated in 43% yield (19.0 mg). *Trans* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.81 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.79 (s, 2H), 4.22 (m, 1H), 2.46 (s, 6H), 2.10 (s, 3H), 1.26 (d, J = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 151.15, 149.84, 148.51, 139.03, 132.56, 131.59, 130.83, 126.91, 126.84, 115.78, 27.97, 24.29, 21.43, 20.23. *Cis* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.16 (d, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.52 (s, 2H), 6.48 (t, J = 8.4 Hz, 1H), 6.22 (d, J = 7.9 Hz, 1H), 3.89 (m, 1H), 2.00 (s, 3H), 1.89 (s, 6H), 1.33 (d, J = 6.7 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.10, 150.84, 145.95, 136.22, 129.74, 129.68, 127.18, 126.11, 125.41, 115.64, 28.54, 23.75, 21.12, 18.12. HRMS m/z calcd for $C_{18}H_{23}N_2$ $[M+H]^+$: 267.1861, found: 267.1852. UV-Vis (mixture of 89% *cis* and 11% *trans*): λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 284 (8000), 329 (8000), ~460 (600); *trans* isomer: λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 331 (16700), ~478 (900).

MesN=N(2-$CH_3C_6H_4$) (5). The reaction was carried out according to the general procedure by reacting 30.0 mg (0.032 mmol) of **2** with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 21.3 mg (0.159 mmol, 5 equiv) of 2-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene **5** was isolated in 36% yield (14.3 mg). *Trans* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.1 (m, 3H), 6.79 (s, 2H), 2.6 (s, 3H), 2.46 (s. 6H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.39, 149.58, 139.10, 138.57, 132.79, 131.88, 131.12, 130.87, 127.07, 115.76, 21.44, 20.40, 18.36. *Cis* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 6.94 (d, *J* = 7.3 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.5 (s, 2H), 6.48 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 2.52 (s, 3H), 1.99 (s, 3H), 1.86 (s, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.68, 152.01, 136.15, 135.39, 131.97, 129.68, 128.98, 126.30, 125.64, 115.83, 30.56, 21.10, 17.96. HRMS m/z calcd for $C_{16}H_{19}N_2$ $[M+H]^+$: 239.1548, found: 239.1539. UV-vis (mixture of 90% *cis* and 10% *trans*): λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 331 (28000), 460 (2000), *trans* isomer: λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 332 (14900), ~480 (500).

MesN=N(2-EtC_6H_4) (6). The reaction was carried out according to the general procedure by reacting 30.0 mg (0.032 mmol) of **2** with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 23.5 mg (0.159 mmol, 5 equiv) of 2-ethylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene **6** was isolated in 34% yield (14.1 mg). *Trans* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.15 (m, 2H), 7.09 (m, 1H), 6.78 (s, 2H), 3.1 (q, *J* = 7.6 Hz, 2H), 2.46 (s, 6H), 2.10 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 151.77, 149.63, 144.59, 139.11, 132.72, 131.41, 130.87,

130.41, 127.13, 115.76, 25.41, 21.43, 20.32, 16.87. *Cis* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.04 (d, *J* = 7.6 Hz, 1H), 6.8 (m. 1H), 6.51 (s, 2H), 6.49 (t, *J* = 8.4 Hz, 1H), 6.23 (d, *J* = 8.2 Hz, 1H), 3.00 (q, *J* = 7.5 Hz, 2H), 2.00 (s, 3H), 1.88 (s, 6H), 1.34 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.12, 141.43, 136.16, 130.11, 129.72, 129.43, 126.19, 125.57, 115.74, 24.83, 21.11, 18.09, 15.06. HR-MS m/z calcd for $C_{17}H_{21}N_2$ $[M+H]^+$: 253.1705, found: 253.1697. UV-vis (mixture of 90% *cis* and 10% *trans*): λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 284 (11600), 330 (13800), 467 (1100), *trans* isomer: λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 286 (sh, 6500), 331 (12000), 472 (500).

(2,6-$Et_2C_6H_3$)N=N(2-^{i}PrC_6H_4) (7). The reaction was carried out according to the general procedure by reacting 30.0 mg (0.032 mmol) of **2** with 28.0 mg (0.159 mmol, 5 equiv) of 2,6-diethylphenyl azide and 25.8 mg (0.159 mmol, 5 equiv) of 2-*i*propylphenyl; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene **7** was isolated in 37% yield (17.2 mg). *Trans* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.03 (m, 2H), 6.98 (m, 2H), 4.2 (m, 1H), 2.69 (q, *J* = 7.3 Hz, 4H), 1.20 (d, *J* = 7.0 Hz, 6H), 1.09 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.27, 150.95, 148.83, 137.27, 132.01, 128.94, 127.03, 27.74, 26.01, 24.40, 16.32. *Cis* isomer: 7.12 (m, 2H), 6.91 (m, 1H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.42 (m, 1H), 6.24 (d, *J* = 9.1 Hz, 1H), 3.95 (m, 1H), 2.36 (m, 2H), 2.07 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 6H), 0.95 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 151.54, 148.74, 146.83, 137.94, 134.15, 131.86, 131.77, 129.45, 127.36, 127.32, 127.15, 126.97, 125.34, 115.81, 28.45, 24.85, 23.82, 14.07. HR-MS m/z calcd for $C_{19}H_{25}N_2$ $[M+H]^+$: 281.2018, found: 281.2010. UV-vis (84% *cis* and 16% *trans* mixture): λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 283 (7050), 314 (8500), 469 (950), *trans* isomer: λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 331 (20000), 479 (460).

(2,6-$Et_2C_6H_3$)N=N(2-MeC_6H_4) (8). The reaction was carried out according to the general procedure by reacting 30.0 mg (0.032 mmol) of $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ catalyst with 28.0 mg (0.159 mmol, 5 equiv) of 2,6-diethylphenyl azide and 21.3 mg (0.159 mmol, 5 equiv) of 2-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene **8** was isolated in 25% yield (10.5 mg). *Trans* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.77 (d, J = 7.2 Hz, 1H), 7.08 (m, 4H), 7.02 (m, 2H), 2.74 (q, J = 7.3 Hz, 4H), 2.6 (s, 3H), 1.14 (t, J = 7.5 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.25, 151.93, 138.71, 137.54, 132.03, 131.52, 129.06, 128.31, 127.17, 26.13, 18.23, 16.42. *Cis* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 6.94 (m, 2H), 6.82 (d, J = 7.6 Hz, 2H), 6.73 (t, J = 7.5 Hz, 1H), 6.47 (t, J = 7.8 Hz, 1H), 6.26 (d, J = 7.9 Hz, 1H), 2.56 (s, 3H), 2.38 (m, 2H), 2.08 (m, 2H), 0.98 (t, J = 7.5 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.09, 136.20, 129.23, 128.47, 127.26, 126.88, 125.62, 116.07, 115.83, 32.30, 24.70, 23.39, 18.00, 14.68, 14.07. HR-MS m/z calcd for $C_{17}H_{21}N_2$ $[M+H]^+$: 253.1705, found: 253.1699. UV-vis (75% *cis* and 25% *trans* mixture): λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 285 (sh, 20100), 318 (20700), 461 (1700), *trans* isomer: λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 321 (14300), 476 (730).

MesN=N(2,6-$Et_2C_6H_4$) (9). The reaction was carried out according to the general procedure by reacting 30.0 mg (0.032 mmol) of $Fe(OC^tBu_2(3,5\text{-}Ph_2C_6H_3))_2(THF)_2$ catalyst with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 27.9 mg (0.159 mmol, 5 equiv) of 2,6-diethylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 16% yield (7.2 mg). *Trans* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 7.09 (m, 1H), 7.04 (m, 2H), 6.78 (s, 2H), 2.73 (q, J = 7.6 Hz, 4H), 2.48

(s, 6H), 2.09 (s, 3H), 1.15 (t, J = 7.5 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 152.37, 149.57, 139.44, 137.20, 132.86, 131.04, 130.29, 128.81, 26.08, 21.38, 20.47, 16.71. *Cis* isomer: ^{1}H NMR (600 MHz, C_6D_6) δ 6.93 (m, 1H), 6.82 (d, J = 7.6 Hz, 2H), 6.48 (s, 2H), 2.73 (q, J = 7.6 Hz, 4H), 1.95 (s, 3H), 1.92 (s, 6H), 1.00 (t, J = 7.6 Hz, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 153.81, 152.15, 137.52, 133.81, 127.13, 25.31, 21.04, 19.24, 14.39. HR-MS m/z calcd for $C_{19}H_{22}N_2$ $[M+H]^+$: 281.2018, found: 281.2011. UV-vis (67% *cis* and 33% *trans* mixture): λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 259 (14900), 287 (11000), 459 (2000), *trans* isomer: λ_{max}, nm (ε_M, $Lmol^{-1}cm^{-1}$): 312 (13000), 473 (1100).

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The authors declare no competing financial interests.

The Supporting Information is available: ^{1}H NMR and GC-MS spectra of the crude products, ^{1}H and ^{13}C NMR, UV-vis, and HRMS spectra of the purified compounds **4-9**, and additional experimental details.

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TOC entry

Iron(II) bis(alkoxide) catalyst enables heterocoupling of bulky aryl nitrenes to produce asymmetric azoarenes that exhibit clean *cis-trans* interconversion under different conditions.