Amination of Benzylic C–H Bonds by Arylazides Catalyzed by Co^{II}–Porphyrin Complexes: A Synthetic and Mechanistic Study

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Abstract: Co^{II}–porphyrin complexes catalyze the reaction of aromatic azides (ArN_3) with hydrocarbons that contain a benzylic group (ArR^1R^2CH) to give the corresponding amines ($ArR^1R^2C{-}NHAr$). When at least one of the R substituents is hydrogen, the catalytic reaction proceeds further to give the imine ArRC=NAr in good yields. The reaction mechanism has been investigated. The reaction proceeds through a reversible coordination of the arylazide to the Co^{II}–porphyrin complex. This unstable adduct can either react with the hydrocarbon in the rate-determining step or decompose by a unimolecular mechanism to afford a putative "nitrene" complex, which reacts with more azide, but not with the hydrocarbon, to afford the byproduct diaryldiazene. The kinetics of the catalytic reaction have been investigated for a range of azides and substituted toluenes. Arylazides with electron-withdrawing substituents react at a faster rate and a good correlation is found between the log(k) and the Taft parameters. On the other hand, an excellent correlation between the logarithm of the rate for substituted toluenes relative to that of toluene and a radical parameter ($\sigma^{\cdot}_{JJ}$) alone was found, with no significant contribution by polar parameters. An explanation has been proposed for this anomalous effect and for the very high isotopic effect ($k_H/k_D = 14$) found.

Keywords: amination · azides · C–H activation · cobalt · porphyrinoids

Introduction

The development of intermolecular nitrogen-atom transfer reactions catalyzed by metals, such as the amination of saturated C–H bonds, is a topic of high current interest.[1–10] Reasonably good results have only been obtained by using [*N*(*p*-tolylsulfonyl)imino]phenyliodinane (PhI=NTs),[1–4] chloramine-T,[1, 5] and related derivatives as the nitrogen source. However these compounds can only be obtained from the corresponding sulfonamides,[7] and, thus, they belong to a limited family of reagents. Recently, we developed a methodology for the intermolecular allylic amination of unactivated olefins by nitroarenes in the presence of CO and ruthenium complexes as catalysts.[8] However, in these last reactions only the allylic C–H bond of an olefin could be functionalized.

Aromatic azides (ArN_3) represent a wide class of easily synthesized compounds. We have recently reported that porphyrin complexes of cobalt(II) are able to activate aromatic azides for the amination under mild conditions of allylic C–H bonds,[9] and we report here that the same catalytic system also results in the more difficult activation of the C–H bonds of saturated organic compounds, to give secondary amines and imines. While the use of porphyrin complexes of manganese, iron, and ruthenium as catalysts in the amidation reactions by PhI=NTs has been reported,[2–4] to the best of our knowledge, porphyrin complexes of cobalt(II) have never been employed before as catalysts for these reactions with the exception of the allylic amination of cyclohexene mentioned before.[9, 10] The use of organic azides as aminating agents considerably extends the number of nitrogen-containing organic compounds that can be potentially obtained in catalytic reactions. Such a reaction has never been reported before, apart from our preliminary communication on this topic.[11] It should be also pointed out that although the condensation of ketones with primary amines is a textbook route to ketimines, the procedure is sometimes not practical for the synthesis of aromatic ketimines.[12] Thus other practical routes to imines are desirable to supplement the classical condensation pathway.

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Results

Synthetic results: The reaction of hydrocarbons that contain a benzylic group with *para*-nitrophenylazide catalyzed by Co^{II}–porphyrin derivatives leads to then formation of the corresponding amines [Eq. (1)]. When at least one of the R substituents is hydrogen, the catalytic reaction proceeds further, at least in part, to give the corresponding imine [Eq. (2)]:

$$ArR^1R^2CH + ArN_3 \xrightarrow{Co^{II}-porphyrin} ArR^1R^2C{-}NHAr + N_2 \quad (1)$$

$$ArRHC{-}NHAr + ArN_3 \xrightarrow{Co^{II}-porphyrin} ArRC{=}NAr + ArNH_2 + N_2 \quad (2)$$

The reaction given in Equation (2) has been independently observed by pre-forming the amines p-$YC_6H_4NH{-}CH_2Ph$ and treating them with p-$YC_6H_4N_3$ ($Y = NO_2$, Cl, OMe) in the presence of the catalyst. The reaction quantitatively gives one equivalent of imine and one molecule of p-$YC_6H_4NH_2$ per equivalent of amine, while no reaction is observed in the absence of the catalyst.

Main byproducts of the reaction given in Equation (1) are the azide-derived aniline and the diarylazo compound. Other byproducts should be high-boiling materials, since they could not be identified by gas-chromatography.

The following Co^{II}–porphyrin complexes were tested as catalysts: [Co(tpp)] (tpp = dianion of *meso*-tetraphenylporphyrin), [Co(p-MeOtpp)] (p-MeOtpp = dianion of *meso*-tetrakis-4-methoxyphenylporphyrin), [Co(p-Cltpp)] (p-Cltpp = dianion of *meso*-tetrakis-4-chlorophenylporphyrin), and [Co(oep)] (oep = dianion of *beta*-octaethylporphyrin). The results of a screening of the reactions of toluene with a series of aryl azides bearing different substituents in the *para* position and catalyzed by several porphyrin complexes is reported in Table 1. The results obtained with other benzylic compounds are reported in Table 2.

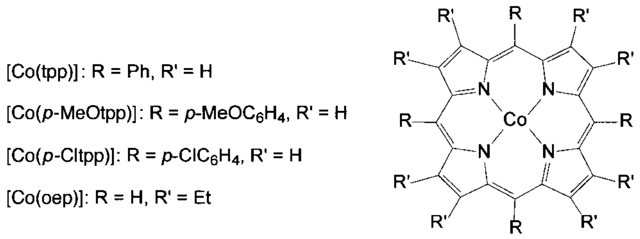


Table 1. Amination of toluene by p-$XC_6H_4N_3$ catalyzed by Co–porphyrin.[a]

Catalyst	X	*t* [h][b]	Imine **2** yield [%][c,d]	Amine **1** yield [%][c]	p-$XC_6H_4NH_2$ yield [%][c]	Diazene **3** yield [%][c]
[Co(tpp)]	NO_2	2	23 (**2a**)	–	28	22 (**3a**)
[Co(tpp)]	OCH_3	10	10 (**2b**)	–	14	25 (**3b**)
[Co(tpp)]	Cl	5	28 (**2c**)	–	29	18 (**3c**)
[Co(tpp)]	H	11	25.5 (**2h**)	–	44.4	18 (**3h**)
[Co(tpp)]	CH_3	12	18 (**2g**)	–	18	38.6 (**3g**)
[Co(tpp)]	F	5	14.9 (**2e**)	–	16.9	49.2 (**3e**)
[Co(tpp)]	Br	8	37.2 (**2f**)	–	44.4	12.1 (**3f**)
[Co(tpp)]	CN	4	37.0 (**2d**)	–	43.1	8.7 (**3d**)
[Co(p-Cltpp)]	NO_2	2	24 (**2a**)	–	31	15 (**3a**)
[Co(p-Cltpp)]	OCH_3	12	6 (**2b**)	–	13	29 (**3b**)
[Co(p-Cltpp)]	Cl	2	25 (**2c**)	–	28	16 (**3c**)
[Co(p-Cltpp)]	H	15	23.8 (**2h**)	–	33.4	14.3 (**3h**)
[Co(p-Cltpp)]	CH_3	15	18.7 (**2g**)	–	27.9	27.2 (**3g**)
[Co(p-Cltpp)]	F	10	27.0 (**2e**)	–	30.5	30.1 (**3e**)
[Co(p-Cltpp)]	Br	7	26.7 (**2f**)	–	43.1	5.7 (**3f**)
[Co(p-Cltpp)]	CN	7	38.0 (**2d**)	5.8 (**1d**)	49.0	– (**3d**)
[Co(p-MeOtpp)]	NO_2	3	21 (**2a**)	–	28	19 (**3a**)
[Co(p-MeOtpp)]	OCH_3	11.5	7 (**2b**)	–	13	20 (**3b**)
[Co(p-MeOtpp)]	Cl	3	35 (**2c**)	–	36	22 (**3c**)
[Co(p-MeOtpp)]	H	10	21.0 (**2h**)	–	39.0	11.2 (**3h**)
[Co(p-MeOtpp)]	CH_3	12.5	18.1 (**2g**)	–	35.9	20.1 (**3g**)
[Co(p-MeOtpp)]	F	6	24.8 (**2e**)	–	25.4	37.2 (**3e**)
[Co(p-MeOtpp)]	Br	4	26.6 (**2f**)	–	39.4	13.4 (**3f**)
[Co(p-MeOtpp)]	CN	2	30.0 (**2d**)	6.1 (**1d**)	48.5	12.1 (**3d**)
[Co(oep)]	NO_2	1	19 (**2a**)	–	23	29 (**3a**)
[Co(oep)]	OCH_3	15	3 (**2b**)	–	10	24 (**3b**)
[Co(oep)]	Cl	4	20 (**2c**)	–	20	22 (**3c**)
[Co(oep)]	H	11.5	18.2 (**2h**)	–	36.1	15.8 (**3h**)
[Co(oep)]	CH_3	13	21.7 (**2g**)	–	33.0	27.2 (**3g**)
[Co(oep)]	F	5	17.6 (**2e**)	–	17.6	59 (**3e**)
[Co(oep)]	Br	3.5	25.8 (**2f**)	–	32.9	9.7 (**3f**)
[Co(oep)]	CN	2	32.5 (**2d**)	22.7 (**1d**)	38.5	2.6 (**3d**)

[a] Experimental conditions: arylazide = 1.40 mmol, molar ratio arylazide/Co = 100:1, in refluxing toluene (20 mL). [b] Time required to reach the complete conversion of the azide. [c] Determined by gas-chromatographic analysis. [d] Note that for the imine the reaction requires two moles of azide per mole of the imine and thus the maximum yield in imine is 50%.

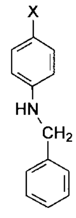
Note that the stoichiometry in the reactions in Equations (1) and (2) implies that a maximum yield of 50% can be obtained with respect to the arylazide when the imine is the product.

The reaction is sensitive to the nature of the azide employed. With toluene as substrate, only in the case of p-cyanophenylazide was the benzylamine observed among the products (Table 1). In all other cases, the reaction in Equation (2) was so fast relative to that in Equation (1) that no benzylamine could be detected at any stage of the reaction. With all catalysts, electron-withdrawing substituents in the *para* position of the aromatic azide generally increased the yields of the imine, except for the derivatives having the p-NO_2 group, which consistently gave lower selectivities than expected based on the general trend. It should be noted that imines with the p-nitro substituent hydrolyses very easily even during the workup and gas-chromatographic analysis; this at least partly explains the lower selectivity observed with respect to that expected based on the high electron-withdrawing power of the nitro group. If the data for the p-NO_2 group are neglected, a fair correlation ($0.632 < R^2 < 0.831$) between the imine selectivity and the Hammet σ constants is observed for all catalysts and an even better correlation ($0.721 < R^2 < 0.956$) is observed with the σ^+ constants (Figure 1 and Figures S1–S4 in the Supporting Information). Moreover, the slope of the lines derived from the linear regression of the selectivity versus σ^+ plots are quite close to each other (20.9, 21.5, 17.4, and 18.8 for [Co(tpp)], [Co(p-Cltpp)], [Co(p-MeOtpp)] and [Co(oep)], respectively). It should be stressed that, on theoretical grounds, no linear correlation is in general to be expected between a selectivity value and the σ or σ^+ constants. However, the fact that such a correlation is indeed observed and the similarity of the slopes for different catalysts has some, at least qualitative, mecha-

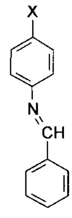
Table 2. Catalytic amination of benzylic compounds by p-$O_2NC_6H_4N_3$.

Entry	Catalyst	Substrate	t [h][a]	Imine yield [%][b]	Amine yield [%][b]	p-Nitroaniline yield [%][b]	Diazene **3a** yield [%][b]
1[c]	[Co(tpp)]	isopropylbenzene	1.5	–	15.8[d](**4**)	23[d]	8[d]
2[c]	[Co(oep)]	isopropylbenzene	6	–	27.2[d](**4**)	28[d]	14[d]
3[c]	[Co(p-MeOtpp)]	isopropylbenzene	2	–	42.3[d](**4**)	24[d]	5[d]
4[c]	[Co(p-Cltpp)]	isopropylbenzene	5.5	–	52.7[d](**4**)	20[d]	15[d]
5[c]	[Co(tpp)]	*sec*-butylbenzene	4	–	15.0[d](**5**)	8[d]	21[d]
6[c]	[Co(oep)]	*sec*-butylbenzene	5	–	13.6[d](**5**)	24[d]	10[d]
7[c]	[Co(p-MeOtpp)]	*sec*-butylbenzene	5	–	10.3[d](**5**)	23[d]	11[d]
8[c]	[Co(p-Cltpp)]	*sec*-butylbenzene	3	–	12.2[d](**5**)	40[d]	10[d]
9[c]	[Co(tpp)]	cyclohexylbenzene	2.5	–	28.3[d] (**6**)	42.1[d]	22.8[d]
10[c]	[Co(tpp)]	ethylbenzene	3	25[e](**7**)	13[e](**8**)	29[e]	11[e]
11[c]	[Co(oep)]	ethylbenzene	1	18[e](**7**)	22[e](**8**)	21[e]	11[e]
12[c]	[Co(p-MeOtpp)]	ethylbenzene	3.5	24[e](**7**)	22[e](**8**)	26[e]	10[e]
13[c]	[Co(p-Cltpp)]	ethylbenzene	4	19[e](**7**)	25[e] (**8**)	33[e]	2[e]
14[c]	[Co(tpp)]	diphenylmethane	3	11.4[e](**9**)	55.2[e](**10**)	24[e]	–
15[f]	[Co(tpp)]	fluorene	6	39.2[d](**11**)	–	41[d]	12[d]
16[f]	[Co(oep)]	fluorene	2.5	41.4[d](**11**)	–	43[d]	4[d]
17[f]	[Co(p-MeOtpp)]	fluorene	5	36.9[d](**11**)	–	42[d]	8[d]
18[f]	[Co(p-Cltpp)]	fluorene	8	38.4[d](**11**)	–	40[d]	9[d]
19[f]	[Co(tpp)]	9,10-Dihydroanthracene	12	32[g](**12**)	–	46[e]	–

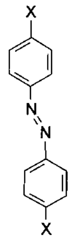
[a] Time required to reach the complete conversion of the aromatic azide. [b] Calculated with respect to converted azide. Note that for the imine the reaction requires two moles of azide per mole of the imine and thus the maximum selectivity in imine is 50%. [c] Reactions carried out in the substrate as solvent, T = 110 °C with catalyst/azide = 1:100. [d] Determined by flash chromatography. [e] Determined by gas-chromatographic analysis. [f] Reactions carried out in refluxing benzene, with catalyst/azide/hydrocarbon = 1:100:100. [g] Determined by gas-chromatographic analysis after hydrolysis of the diimine **12** to the diketone **13**. The diimine **12** can be reduced in the same pot to the diamine **14** by $NaBH_4$ (28% total yield).



1d



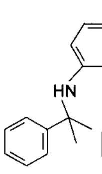
2a-h



3a-h

X =

a: NO_2
b: OCH_3
c: Cl
d: CN
e: F
f: Br
g: CH_3
h: H



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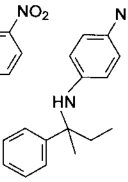

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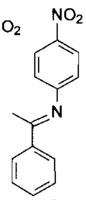

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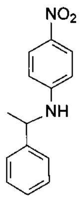

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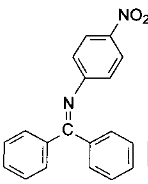

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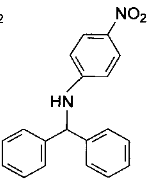

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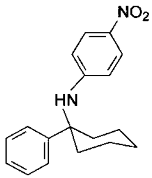

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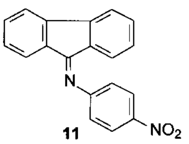

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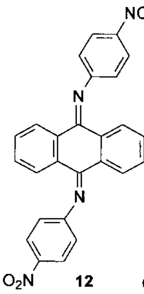

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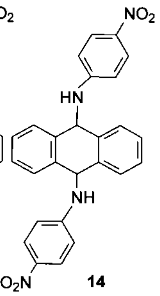

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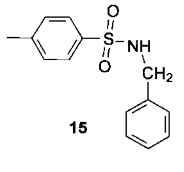

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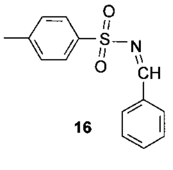

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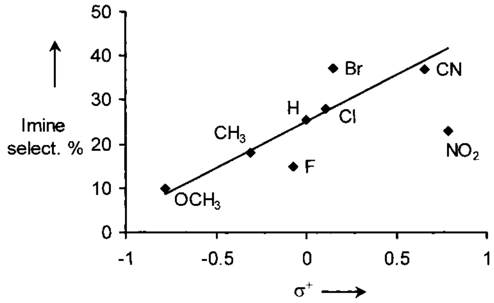

Figure 1. Imine selectivity [%] versus σ^+ constants of the R groups for the reactions of toluene with p-$RC_6H_4N_3$, catalyzed by [Co(tpp)]. See Table 1 for experimental conditions. The line drawn corresponds to the best fit of the equation: imine selectivity [%] = $a\sigma^+ + b$ (a = 20.9, b = 25.2, R^2 = 0.759), for all substituents except NO_2.

nistic implications that will be discussed later, apart from being a useful predicting tool from a synthetic point of view. The similarity of these plots also indicates that there is no statistically significant difference among the results obtained with the various porphyrins. Thus the identity of the porphyrin appears to play only a minor role in the reaction.

All catalysts gave comparable yields for the imine of fluorene (Table 2), whereas [Co(p-Cltpp)] gave the highest yields of amine when isopropylbenzene was used as substrate, although the time needed to reach a complete conversion of the aromatic azide was 3.5 times longer than that required when [Co(tpp)] is used as catalyst. However, it should be noted that for other substrates different orders of activity/selectivity were observed for the same catalysts. For these other substrates, data is insufficient for a statistical treatment, but it is clear that any generalization is premature.

Steric hindrance lowers the selectivity, but does not prevent the reaction and with *sec*-butylbenzene the amine was formed in 10–15% yield (Table 2). A better yield of 28.3% was obtained for the cyclohexylbenzene derived amine.

If the amine is the desired product, in those cases in which the imine is the only or predominant product, the latter can be reduced in situ by $NaBH_4$ before isolation, as shown, for example, by the case of the 9,10-dihydroantracene-derived imine.

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The influence of the hydrocarbon concentration on the selectivity has been investigated by employing toluene and p-$O_2NC_6H_4N_3$ as substrates, with benzene as a diluting solvent. The results, reported in Table 3, clearly show that best results are obtained in neat toluene, and increasing the benzene fraction at constant total volume decreases the imine (**2a**) yield and increases that of the diazene (**3a**). For these reactions, the amount of benzaldehyde formed by hydrolysis of the imine during the reaction or the analysis has also been measured. Some of these reactions were repeated to follow the formation of the products as a function of time. In general, the ratio between the relative formation rates for the different products is approximately constant through all the reaction, that is, no product is formed preferentially at the beginning of the reaction (see Figure S5 in the Supporting Information for one example).

Table 3. Influence of the toluene concentration on the selectivity of the amination of toluene by p-$O_2NC_6H_4N_3$ catalyzed by [Co(tpp)].[a]

Toluene [mL]	Toluene [M]	Imine **2a** yield [%][b,c]	PhCHO yield [%][b]	p-$O_2NC_6H_4NH_2$ yield [%][b]	Diazene **3a** yield [%][b]
3	2.82	12.8	1.8	20.0	67.2
5	4.69	17.1	2.4	28.6	46.8
7	6.57	27.1	3.9	33.6	39.2
10	9.39	29.5	4.5	34.5	36.0

[a] Experimental conditions: arylazide = 0.622 mmol, molar ratio arylazide/Co = 15:1, in toluene/benzene (total volume 10 mL) at 75 °C. Reactions were run up to complete conversion of the azide. [b] Determined by gas-chromatographic analysis. [c] Note that for the imine the reaction requires two moles of azide per mole of the imine and thus the maximum yield in imine is 50%.

Since most metal–porphyrin catalyzed amination reactions reported up to date afford the sulfonylamide as product, we also investigated the use of TsN_3 and TsN=IPh as aminating agents. Tosylazide gave a very slow reaction. After 24 hours in refluxing toluene ([Co(tpp)] as catalyst, experimental conditions as in Table 2), only a 68.5% conversion was observed. The imine **16** was formed with a 28.2% selectivity, together with the corresponding saturated amine **15** (21.5%) and tosylamide ($TsNH_2$, 39.5%). Tosyliminoiodinane was even less reactive and afforded only trace amounts (as detected by GC-MS) of benzylic amine and imine; the only product detected in large amounts was $TsNH_2$.

Mechanistic study: To clarify the mechanism of this reaction we performed some stoichiometric reactions and a kinetic study. No reaction is observed between [Co(tpp)] and toluene or between the azide and toluene alone, even at reflux temperature. On the other hand, when [Co(tpp)] was treated with excess p-$O_2NC_6H_4N_3$ at 75 °C in benzene, the diazoarene p-$O_2NC_6H_4N{=}NC_6H_4NO_2$-$p$ was catalytically obtained. When the same reaction was repeated at a lower temperature in C_6D_6, new signals were observed in the ^1H NMR spectrum that cannot be attributed to any know compound, but are identical to the ones of the product obtained by reaction of [Co(tpp)] with p-$O_2NC_6H_4N{=}NC_6H_4NO_2$-$p$. Observation of only one set of resonances for the aryl groups of the ArN=NAr moiety of this complex indicates that the aromatic groups of the "ArN" moieties are equivalent, at least on the ^1H NMR timescale. An analogous result is observed when [Co(p-MeOttp)] is used in place of [Co(tpp)]. Examination of the same reactions by UV-visible spectroscopy also indicates the identity of the final products when the azide or the diazene is employed as starting material. At least one complex has been reported in the literature that has an unsubstituted diazene (HN=NH) group bridging two ruthenium–porphyrin moieties.[13] An analogous formulation as [{Co(porphyrin)}$_2$(ArN=NAr)] (porphyrin = tpp or p-MeOtpp, Ar = p-$NO_2C_6H_4$) would also be consistent with our spectroscopic data, but all attempts to grow single crystals suitable for X-ray diffraction always gave the Co–porphyrin complex without additional ligands. Thus it is possible that the observed shift in the signals of the aryldiazene is only due to the proximity of the paramagnetic cobalt complex, rather than to a true coordination. If any coordination is present, it must be very weak, as also indicated by the fact that addition of aryldiazene to the catalytic reaction mixture does not slow down the reaction (see later). An analogous outcome was observed when [Co(tpp)] was treated with p-$MeOC_6H_4N_3$. With the sterically bulky azides Ph_3CN_3 and adamantylazide no reaction was observed. With p-$CF_3C_6H_4N_3$; another reaction prevailed, leading to fluorine loss from the CF_3 group and formation of a complex that appears to be [Co(tpp)F][14] based on the spectroscopic data. This reaction was not investigated further.

It should be noted that the signals due to the porphyrin in the ^1H NMR spectrum are immediately broadened when p-$O_2NC_6H_4N_3$ or p-$MeOC_6H_4N_3$ (but not Ph_3CN_3 or adamantylazide) are added, regaining the original shape after the azide has been completely consumed. This suggests a reversible interaction of the azide with the cobalt complex.

The reaction of p-$O_2NC_6H_4N_3$ with toluene catalyzed by Co–porphyrin complexes is practically suppressed when carried out in the presence of the spin-trap compound TEMPO (2,2,6,6-tetramethyl-1-pyperidine-*N*-oxide). Since there is no reaction between the Co–porphyrin complexes and TEMPO in the absence of the azide, this suggests that the unpaired spin density of the Co–porphyrin complex is partly localized on the azide nitrogen atoms in the intermediate complex.[15]

A kinetic study was also performed by employing p-$O_2NC_6H_4N_3$ and toluene as substrates and [Co(tpp)] as catalyst. The reaction was followed by IR spectroscopy, monitoring the intensity of the 2120 cm^{-1} absorption of the arylazide. All reactions showed an excellent first-order dependence of the rate on azide concentration ($R^2 > 0.98$ for all reactions). The rate was unaffected by the addition of the products of the reaction (imine, diazene, nitroaniline), an indication that the observed kinetics is not an effect of product inhibition; this is known in some cases to afford plots easily mistaken for first-order behavior in one of the reagents. The kinetics are also first-order with respect to [Co(tpp)] (Figure S6, Supporting Information), but shows a saturation behavior with respect to toluene concentration, the other solvent being benzene (Figure 2). All kinetic experiments in this paper were run at 75 °C to avoid boiling of benzene in those reaction in which it was present.

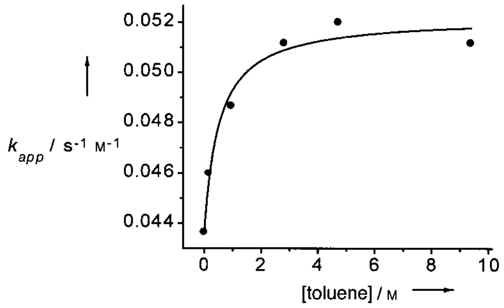


Figure 2. Influence of the toluene concentration on the value of k_{app} [s^{-1}M^{-1}] in the equation: $-d[ArN_3]/dt = k_{app}[[Co(tpp)]][ArN_3]$ (Ar = p-$O_2NC_6H_4$–); $T = 75\,°C$. The line drawn corresponds to the best fit for Equation (6).

When the selectivity was examined as a function of time for different toluene/benzene mixtures the following observations were made.

1) The amount of imine and p-nitroaniline grow at the same rate, in accord with the stoichiometry reported in the reactions in Equations (1) and (2).
2) The rate of formation of p-$O_2NC_6H_4N{=}NC_6H_4NO_2$-$p$ is proportional to the one of the imine for each reaction, indicating the same dependency from the azide concentration (for one example see Figure S5, supporting information).
3) The rate of formation (and the final selectivity, Table 3, Figure 3) of imine increases with the toluene concentration (up to 100 % toluene in the solvent mixture), while the one of the diarylazo compound decreases in the same series, indicating a common intermediate and a competition for the formation of the two products.

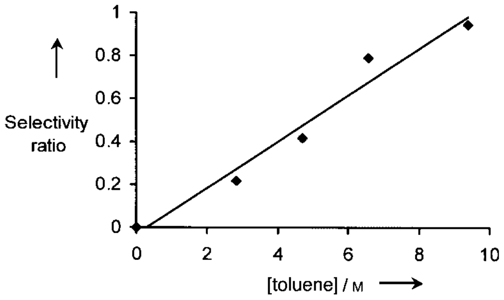


Figure 3. Influence of the toluene concentration on reaction selectivity. Selectivity ratio = (imine + aldehyde selectivity)/diazene selectivity. Relevant data are reported in Table 3. The line drawn corresponds to the best fit for the equation: selectivity ratio = k_2[toluene]/$2k_3$ with $k_2/2k_3 = 0.108$ ($R^2 = 0.965$).

Two further kinetic series were measured. In the first, toluene was kept constant as a substrate, and the reaction rate for different azides was measured. In the second, differently *para*-substituted toluenes were compared, keeping the azide constant.

As far as the series of the azides is concerned, a fair correlation was observed between the log of the ratio between the rate of the amination reaction with the substituted azides and the rate of the corresponding reaction with phenylazide and the Hammet σ constant (Figure S7, Supporting Information), with $\rho = 0.68$ ($R^2 = 0.71$). Attempts to improve the correlation quality by performing a dual parameter analysis introducing also a radical parameter ($\sigma^{\bullet}_{JJ}$, see later) left the R^2 value essentially unchanged; however, a better correlation was observed if the Taft parameters,[16] which allow a separate description of field and resonance effects, were employed (Figure 4).[17] The best fit for the equation: $\log(k_{ArN_3}/k_{PhN_3}) = \rho_F\sigma_F + \rho_R\sigma_R + c$ was found for the values $\rho_F = 1.086$ and $\rho_R = 0.209$ ($R^2 = 0.882$).

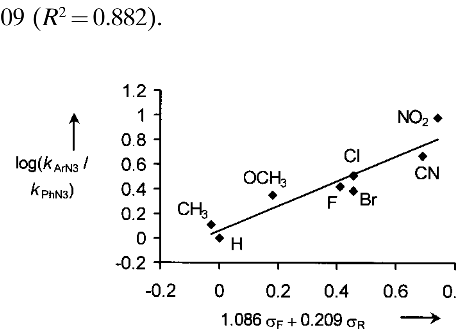
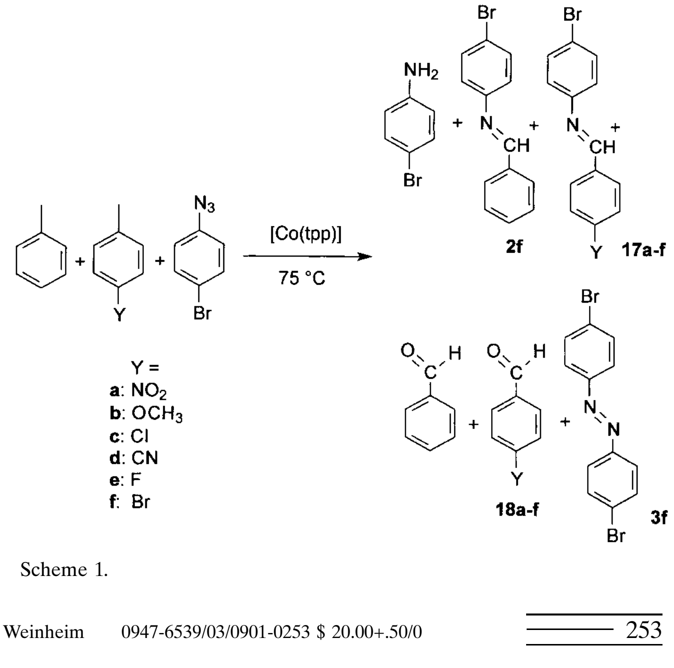


Figure 4. Linear free energy correlation of $\log(k_{ArN_3}/k_{PhN_3})$ versus Taft σ_F and σ_R parameters. The best fit for the equation $\log(k_{ArN_3}/k_{PhN_3}) = \rho_F\sigma_F + \rho_R\sigma_R + c$ was found for the values $\rho_F = 1.086$ and $\rho_R = 0.209$ ($R^2 = 0.882$).

For the series of the substituted toluenes, we employed p-bromophenylazide as the aminating agent, because some of the imines derived from p-nitrophenylazide hydrolyzed very easily. However, even with p-bromophenylazide a small amount of hydrolysis was observed. Since imine hydrolysis produces the substituted toluene-derived aldehyde and this aldehyde cannot form in any other way, the total amount of imine initially formed was obtained by summing the moles of imine detected by GC with those of the corresponding aldehyde determined by the same technique. Benzylamine was not detected in any of the reactions in this series, whereas p-bromophenyldiazene was always the main byproduct; the identity of which does not depend on the toluene derivative employed. Given the nonlinear dependence of the rate on the toluene concentration, competition reactions were run between the azide and an equimolar mixture of toluene and a substituted toluene (Scheme 1).



Scheme 1.

Since the amount of the two toluenes vary very little during the reaction, the relative rate was determined by the ratio of the products, as in Equation (3):

$$k_r = ([\text{substituted imine}] + [\text{substituted benzaldehyde}])/([\text{unsubstituted imine}] + [\text{benzaldehyde}]) \quad (3)$$

We note that this equation holds because no other toluene-derived product was obtained except for those mentioned. In particular, no dibenzyl or other products derived from free-radical reactions were observed in any case.

No correlation at all is found between the log k_r values for the substrates reported in Scheme 1 and the Hammet σ or the related σ^+ constants. In the literature, it has been reported that the rates of analogous benzylation reactions by p-toluensulfonyliminoiodinane are sensitive to radical stabilization effects, which are scarcely reproduced by the aforementioned constants. A good correlation could be obtained[4a,c,f] by either the use of a parameter called "total effect" (TE),[18] which takes into accounts both polar and radical effects, or by a multivariate analysis,[19] in which a constant was employed that only describes the radical effects ($\sigma^{\bullet}_{JJ}$), together with the standard Hammet σ (or the modified σ^+) constant to describe the polar contribution. In our system, use of the TE parameter in place of σ improved the correlation a bit, which remained poor; however, an excellent agreement with the experimental data was obtained by use of the $\sigma + \sigma^{\bullet}_{JJ}$ multivariate correlation.

Equation (4), with $\rho^{\bullet}_{JJ} = 1.25$, $\rho = 0.00961$ and $c = 0.0322$, describes the experimental values with $R^2 = 0.9887$ (Figure 5).

$$\log k_r = \rho^{\bullet}_{JJ}\sigma^{\bullet}_{JJ} + \rho\sigma + c \quad (4)$$

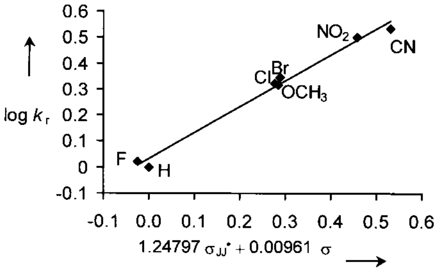


Figure 5. Linear free energy correlation of $\log k_r$ [as defined in Eq. (4)] versus ($\sigma^{\bullet}_{JJ}$, σ). The best fit for the equation $\log k_r = \rho^{\bullet}_{jj}\sigma^{\bullet}_{JJ} + \rho\sigma + c$ was found for the values $\rho^{\bullet}_{JJ} = 1.24797$ and $\rho = 0.00961$ ($R^2 = 0.9887$).

The overwhelming importance of the radical parameter is completely unprecedented. Indeed, the contribution of the polar parameter is so small (0.8 % of that of the radical) that neglecting it completely (and fitting the data only to $\sigma^{\bullet}_{JJ}$) gives an indistinguishably good fit ($R^2 = 0.9885$ instead of 0.9887, with $\rho^{\bullet}_{JJ} = 1.26$, Figure S8 in the Supporting Information). This anomaly will be discussed later.

The isotopic effect on the benzylation reaction was measured by running a reaction analogous to the preceding ones, but with deuterated toluene in place of the substituted toluene. Determination of the relative amounts of deuterated products was made by integration of the masses of the peaks observed in the GC-MS spectrum of the solution after the reaction. The primary isotopic effect determined, $k_H/k_D = 14$ is again a value outside the normal range (usually 1–7).

Discussion

Synthetic aspects: In this paper we have reported on a new reaction strategy for the amination of benzylic C–H bonds, leading to amines and imines. Although much work has still to be done before such a strategy will be fully developed, a few points are worth being evidenced here.

While the synthesis of *N*-alkylanilines continues to attract much attention,[20] very few analogues of the *N*-tertiaryalkylanilines here described have been reported in the literature,[21] and the synthesis of several of them required several steps and the use of reagents such as BuLi and PhLi, which are incompatible with most functional groups.

The synthesis of imines is generally performed by reaction of amines or other compounds derived from them with carbonyl compounds. The method gives excellent results in some cases, but is unsatisfactory in others, most notably in those in which the amine bears electron-withdrawing substituents. In contrast, imines of this kind are those for which the best selectivities are observed with our method. Moreover, our reaction employs the hydrocarbon, rather then the corresponding carbonyl compound, as a substrate. This point is likely to make a difference when only the hydrocarbon is available, since the selective oxidation of a benzylic CH$_2$ group to carbonyl is not an easy reaction.

In situ reduction of imines to the corresponding amines by NaBH$_4$ and related reagents is widely reported in the literature and also works well in the present system.

Concerning the substrates containing the tosyl group, there is no evident reason for the low reactivity of tosylazide under these conditions. A possible explanation is that one oxygen atom of the sulfonyl group interacts with the cobalt center in preference to the azide nitrogen, thus inhibiting the catalytic reaction. The accumulation of an amount of benzylic amine much larger than in any reaction with arylazides can be attributed to the high electron-withdrawing power of the tosyl group. The fast conversion of the benzylic amine to the imine is clearly due to the activating power of an electron-rich heteroatom directly attached to the benzylic carbon on the reactivity of the remaining C–H bonds. The presence of a strongly electron-withdrawing tosyl group is expected to decrease this activation. The very low reactivity of TsN=IPh in the [Co(tpp)]-catalyzed reaction is surprising, since this compound is the standard aminating agent in most metal-catalyzed amination reactions of hydrocarbons. This inactivity points to a different reaction mechanism for cobalt porphyrins with respect to the one observed with other metals, in accord with the following discussion.

Reaction mechanism: It is well known that arylazides generate free nitrenes upon photochemical activation,[22] and, when a metal is present, metal-nitrene (imido) intermediates are generally supposed to be formed. However, in the present case, the kinetic data discount this eventuality. In

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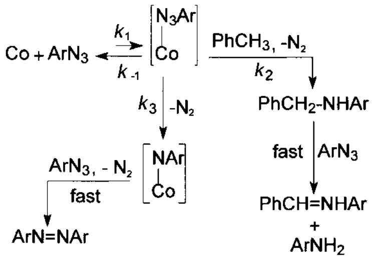
particular, a slow formation of an imido complex followed by a fast reaction of this complex with toluene would give zero-order kinetics with respect to toluene. On the other hand, a fast formation of the imido complex followed by a slow reaction with toluene would give zero-order kinetics with respect to the azide. Moreover, in the latter case, the intermediate complex should be at least spectroscopically observable in solution during the reaction. None of these conditions fit the experimental data.

All of the kinetic data, on the other hand, can be explained by the reaction pathway shown in Scheme 2. Application of



Co = [Co(tpp)]; Ar = p-$NO_2C_6H_4$

Scheme 2.

the steady-state approximation to the intermediate arylazide-porphyrin complex leads to Equation (5):

$$k_{app} = 2k_1(k_2[\text{toluene}] + k_3)/(k_2[\text{toluene}] + k_3 + k_{-1}) \quad (5)$$

which nicely fits the reaction rates observed at different toluene concentrations, as shown in Figure 2. The fitting affords the value $k_1 = 2.6 \times 10^{-2}\,s^{-1}M^{-1}$; however, due to the form of the equation and number of data points, different groups of values for k_2, k_3, and k_{-1} give equally good fittings and the obtained values are not reliable.

In Scheme 2, a reversible interaction occurs between [Co(tpp)] and the arylazide. The equilibrium is shifted towards the side of the starting materials, in accord with the fact that the complex is not observable. This complex can either react with toluene, to afford the benzylamine, or lose dinitrogen in an unimolecular reaction, to afford another intermediate, formulated as a true imido complex, that is responsible for the formation of the aryldiazene in a fast reaction. Formation of the aryldiazene by reaction of a second molecule of azide directly with the same azide complex that reacts with toluene is not consistent with the experimental data. Indeed, such a scenario would imply a non-first-order kinetics with respect to the azide for the formation of the diazene; this would alter the global kinetics observed. Moreover, the concentration of toluene is approximately constant during the reaction, whereas the one of the azide decreases. Thus a direct competition of toluene and azide for the same intermediate would result in a preferential formation of the aryldiazene at the beginning of the reaction, whereas the selectivities in aryldiazene and imine are constant during the reaction (Figure S5, Supporting Information). The constant selectivity during the reaction also excludes that the benzylamine can be formed *both* from the azide complex *and* the imido complex. Again this would imply a higher selectivity in aryldiazene at the beginning of the reaction.

The scenario in Scheme 2 implies that the rate of formation of the imine is proportional to k_2[toluene][[Co(tpp)(ArN_3)] and the one of the diazene is proportional to $2k_3$[[Co(tpp)(ArN_3)]. Since the concentration of the intermediate is the same for both reactions, the ratio between the corresponding selectivities will equal the one between the formation rates. Thus it follows that a linear relation is expected between the ratio of the two selectivities and the toluene concentration, as in Equation (6).

$$\text{Imine selectivity/diazene selectivity} = k_2[\text{toluene}]/2k_3 \quad (6)$$

The results of the experiments run at different toluene concentrations have been reported in Table 3. Since **2a** partly hydrolyzes even during the analysis, the selectivity of the initially formed imine is considered to be the sum of the imine and benzaldehyde selectivities. By plotting the ratio between the (initial) selectivities in imine and diazene against the molar concentration of toluene for the data in Table 3 (also including the origin), a good linear correlation is indeed observed with $k_2/2k_3 = 0.108$ and $R^2 = 0.965$ (Figure 3). This further corroborates the kinetic model employed.

It should be noted that, to the best of our knowledge, the proposal of an arylazide complex as the aminating agent is unprecedented; however, structurally related N-bound tosyliminoiodinane complexes have been proposed on a kinetic ground as the active intermediates in both the Mn/salen-catalyzed sulfimidation of sulfides[23] and in the Mn/porphyrin-catalyzed aziridination of olefins.[24] The latter intermediate was also proposed to be involved in the amidation of saturated C–H bonds by the same catalytic system, based on the observation of a peak ascribable to the fragment [Mn(porphyrin)(PhINTs)]$^+$ in the mass spectrum of the reaction mixture of [Mn(porphyrin)(OH)(MeOH)] with PhINTs.[3]

More information on the reactivity of the arylazide complexes could be gained by the kinetic experiments run with different azides and toluenes. Concerning the azides series, the values obtained for the Hammet and Taft correlation indicate that the nitrogen atom of the azide acts as an electrophile in the transition state, which is not surprising. A fair to good correlation is found even between the imine selectivities and the σ and σ^+ constants. As previously mentioned, no such a linear correlation is to be expected on theoretical grounds. However, the fact that it is observed and the positive slope of both the rate and selectivity correlations indicate that the arylazides reacting faster are also the ones affording the highest selectivities. That both rate and selectivity are favored by electron-withdrawing substituents suggests that the rate-determining step is also the product-determining one. This is in full agreement with the mechanism proposed in Scheme 2 and the mathematical fitting derived from it. Indeed, a faster reaction of the arylazide complex with toluene not only will accelerate the global reaction rate by increasing k_2, but will also increase the selectivity by increasing the ratio k_2/k_3. Evidently, k_3 is probably also affected by the identity of the azide, but it appears to be lesser so than k_2. The close similarity of the slopes of the selectivity versus σ^+ correlations for different catalysts also strongly indicates that the reaction mechanism for all the porphyrin complexes is the same and the validity of Scheme 2 is not limited to [Co(tpp)].

In contrast to the arylazides series, the result of the fit for the toluenes series was completely unexpected. As mentioned before, an excellent correlation was found with a radical parameter alone, with a statistically insignificant contribution of a polar parameter. This situation is anomalous, since the literature data[19] indicate that even in the case of typical radical reactions (e.g., the hydrogen abstraction by a Br$^\bullet$ radical or by *N*-bromosuccinimide) a polar contribution is always present and is generally larger than the radical one. Interestingly, in three cases that we are aware of in which the radical parameter has been reported to be larger than the polar one, the reactions involved are related to the one here discussed, namely, the amidation of saturated C–H bonds by PhI=NTs catalyzed by manganese[3] and ruthenium[4f] complexes and the copper-catalyzed aziridination reaction of substituted styrenes by PhI=NTs.[25] However the difference among the absolute values of the two parameters was quite small in all of these cases. It is worth remembering that the first of these catalytic systems[3] is one of those for which a metal–PhINTs complex was proposed as the active aminating species.

The anomalous importance of radical stabilization effects in the toluene series is paralleled by the very high isotope effect ($k_H/k_D = 14$). This value is clearly higher even of that corresponding to the complete loss of the zero-point energy (about 7 at 25 °C).[26] However, even larger isotopic effects have been previously observed and attributed to a relevant role played by the quantum-mechanical tunneling effect in the reactions under examination.[27] In general, $k_H/k_D > 12$ at 25 °C are considered to be a reliable evidence for tunneling,[27, 28] and the ratio over which tunneling is indicated decreases with an increase in temperature (our value of 14 was measured at 75 °C). The quantum-mechanical tunneling effect can be observed when the reaction involves the transfer of an hydrogen atom that should pass through a very high energy barrier. In these cases, the mass of the atom to be transferred assumes a much greater importance than that the same mass has on the zero-point energy of the bond to be broken. Thus an ^{1}H atom can pass the barrier by tunnel effect much more easily than a deuterium atom will, giving rise to a high observed isotopic effect, which may even be larger than 50.[29]

All of the reactivity and kinetic data point to the transition state shown in Figure 6. For a discussion of alternative coordination modes for the arylazide, see the Supporting Information.[30] The transition state proposed explains all of the kinetic data observed, including the unusual ones. Indeed:

1) The nitrogen atom in the α-position with respect to the aryl ring of the arylazide acts as an electrophile, in accord with the reactivity order of several azides with respect to the Hammet and Taft constants of the *para* substituents.
2) The "pocket" conformation of the arylazide makes steric hindrance very severe for the incoming toluene molecule and prohibits a too close approach of the whole molecule. It must be noted that an increase in the steric hindrance increases the importance of the quantum-mechanical tunneling effect in those systems in which it is present.[31] Using a terminology perhaps not completely rigorous, but chemically intuitive, we can say that steric hindrance prevents the reacting molecules from approaching each other up to the correct distance for the hydrogen-atom transfer to occur in a "classical" way. Thus the hydrogen atom has to do a "long jump" that is characterized by a high-energy barrier, since during the travel it loses most of the stabilization due to the breaking bond, without gaining significantly through the new bond formation. This may well be the case in our system.
3) Apart from the transferred hydrogen atom, the rest of the toluene molecule remains relatively far from the polar nitrogen atom. Since the magnitude of charge interactions depends on the square of the distance, the porphyrin–azide moiety will have only a low polarizing effect on the benzyl group, making charge stabilization on the latter of negligible importance.
4) In the intermediate arylazide complex, part of the unpaired spin density of the paramagnetic cobalt(II) center is likely to be delocalized on the azide ligand. This may explain the inhibition by the radical trap TEMPO, despite that fact that an irreversible reaction between the Co–porphyrin complex and TEMPO in the absence of any arylazide is not observed.

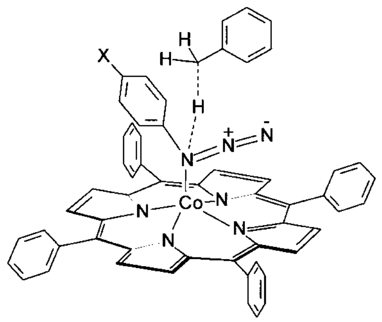


Figure 6. Proposed transition state for the amination reaction.

The only part of the mechanism for which data is insufficient to give a complete picture of the intermediates involved is the one concerning the reaction of the putative "nitrene" intermediate. A speculative explanation of why it only reacts with more arylazide and not with toluene is given in the Supporting Information.[32]

Conclusion

In this paper, we have reported on a new catalytic system for the amination and imination of saturated benzylic C–H bonds by arylazides. Both the synthetic and mechanistic aspects of the reaction have been investigated and some unusual findings have been explained. Yields are in most cases only moderate; however, alternative synthetic strategies require the availability of prefunctionalized starting materials or several steps to reach the same compounds and the total yields are likely to be even lower.

Experimental Section

General procedure: Unless otherwise specified, all reactions and manipulations were performed under an N_2 atmosphere by using standard Schlenk apparatus, cannula techniques, and magnetic stirring. Solvents were dried and distilled by standard procedures and stored under dinitrogen. Arylazides,[33] tpp, *p*-Cltpp, *p*-MeOtpp[34] and their cobalt complexes[35] were synthesized by methods reported in the literature. All other starting materials, including [Co(oep)], were commercial products and were used as received. Concerning the products, all anilines and azobenzene (**3h**) are commercially available. The following products have been previously reported in the literature and have been characterized by comparison of their analytical data with the one reported in the literature or obtained from independently synthesized samples: **1a**,[36] **1b**,[37] **1c**,[38] **1d**,[39] **1e**,[40] **1f**,[41] **1g**,[42] **1h**,[43] **2a**,[44] **2b**,**c**,[42] **2d**,[45] **2e**,[46] **2f**,[47] **2g**,[42] **2h**,[46] **3a**,[48] **3b**–**d**,[49] **3e**,[50] **3f**,[49] **3g**,[51] **4**,[52] **7**,[12a, 53] **8**,[54] **9**,[55] **10**,[56] **11**,[53b] **12**,[57] **15**,[58] **16**,[59] **17a**,[60] **17b**,[61] **17c**,[62] **17d**,[63] **17e**,[64] **17f**.[65] In the following, the ^{1}H NMR spectra of some of them are reported when these data were not available in the literature or when our spectra were of significantly better quality than those reported. Gas chromatographic analyses were performed on a Dani 8610 capillary gas chromatograph equipped with a PS 255 column. R_i values (R_i = response factor, relative to naphthalene as an internal standard) were determined by the use of solutions of known concentrations of the compounds. GC-MS analyses were performed on a Shimadzu GCMS-5000 instrument. NMR spectra were recorded on a Bruker AC 300 FT (300 MHz). IR spectra were recorded on a FTS-7 Bio Rad FT-IR spectrometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

Catalytic reactions: A two-necked flask equipped with a side port and a reflux condenser with a nitrogen inlet on top and kept under N_2 was charged with the solid reagents in a N_2 stream and then the liquid reagents and, if required, the additional solvent was added at RT. The flask was then heated to the desired temperature by a preheated oil bath. For reactions run at reflux, the temperature of the oil bath was set ten degrees higher than the boiling temperature of the solvent. The consumption of the arylazide was monitored by TLC up to the point in which its spot was no longer observable and then by IR spectroscopy. The reaction was considered to be finished when the absorbance of the azide group in the IR spectrum of the solution measured with a 0.5 mm thick cell was at or below 0.03. The so-obtained solution was either analyzed by GC or evaporated to dryness in vacuo and the products separated by flash chromatography on silica. Reagents amounts and reaction times are given in the tables.

Data for compound 4: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 7.94$ (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.44 (d, ^{3}J(H,H) = 7.6 Hz, 2H), 7.37 (dd, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.9 Hz, 2H), 7.28 (dd, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.9 Hz, 1H), 6.30 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 5.07 (s, 1H; NH), 1.73 ppm, (s, 6H; $\mathrm{CH_3}$); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 168.22$, 151.96, 145.78, 132.86, 129.34, 129.22, 127.50, 126.12, 125.68, 30.77 ppm; MS (70 eV, EI): *m*/*z*: 256, 241, 195, 119, 91, 77; elemental analysis calcd (%) for $\mathrm{C_{15}H_{16}N_2O_2}$ (256.3): C 70.29, H 6.29, N 10.93; found: C 70.03, H 6.66, N 10.58.

Data for compound 5: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 7.90$ (d, ^{3}J(H,H) = 8.0 Hz, 2H), 7.40–7.29 (m, 5H), 6.28 (d, ^{3}J(H,H) = 8.0 Hz, 2H), 4.98 (s, 1H; NH), 1.97 (m, ^{3}J(H,H) = 8.2 Hz, 2H; $\mathrm{CH_2}$), 1.69 (s, 3H; $\mathrm{CH_3}$), 0.85 ppm (t, ^{3}J(H,H) = 7.4 Hz, 3H; $\mathrm{CH_3}$); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 152.68$, 149.45, 137.25, 130.10, 127.39, 126.27, 126.17, 113.84, 59.81, 36.91, 25.40, 8.55 ppm; MS (CI): *m*/*z*: 271 [M^{+}+1]; elemental analysis calcd (%) for $\mathrm{C_{16}H_{18}N_2O_2}$ (270.3): C 71.09, H 6.71, N 10.36; found: C 71.42, H 6.53, N 10.27.

Data for compound 6: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 7.92$ (d, ^{3}J(H,H) = 7.9 Hz, 2H), 7.46 (m, 2H), 7.31 (m, 3H), 6.31 (d, ^{3}J(H,H) = 7.9 Hz, 2H), 4.96 (s, 1H; NH), 2.28 (m, 2H), 1.94–1.59 (m, 6H), 0.90 ppm (m, 2H); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 152.31$, 147.05, 138.29, 127.41, 126.98, 126.17, 125.77, 113.93, 58.76, 36.69, 30.11, 22.23 ppm; MS (70 eV, EI): *m*/*z*: 296, 253, 159, 91; elemental analysis calcd (%) for $\mathrm{C_{18}H_{20}N_2O_2}$ (296.4): C 72.95, H 6.80, N 9.45; found: C 73.08, H 6.45, N 9.68.

Data for compound 7: ^{1}H NMR (300MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.26$ (d, ^{3}J(H,H) = 8.0 Hz, 2H), 7.35–7.19 (m, 5H), 6.89 (d, ^{3}J(H,H) = 8.0 Hz, 2H), 2.26 ppm (s, 3H; $\mathrm{CH_3}$); MS (70 eV, EI): *m*/*z*: 240, 225, 207, 179, 163, 117, 76.

Data for compound 8: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.03$ (d, ^{3}J(H,H) = 8.0 Hz, 2H), 7.42–7.25 (m, 5H), 6.48 (d, ^{3}J(H,H) = 8.0 Hz, 2H), 4.63 (s, 1H; NH), 4.59 (q, ^{3}J = 6.8 Hz, 1H; CH), 1.58 ppm (d, ^{3}J(H,H) = 6.8 Hz, 3H; $\mathrm{CH_3}$); MS (70 eV, EI): *m*/*z*: 242, 227, 207, 181, 105, 91, 77.

Data for compound 9: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.03$ (d, ^{3}J(H,H) = 8.4 Hz, 2H), 7.76 (m, 2H), 7.54- 7.28 (m, 6H), 7.15 (m, 2H), 6.81 ppm (d, ^{3}J(H,H) = 8.4 Hz, 2H).

Data for compound 10: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.06$ (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.39–7.28 (m, 10H), 6.50 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 5.63 (d, ^{3}J(H,H) = 3.6 Hz, 1H; CH), 5.00 ppm (d, ^{3}J(H,H) = 3.6 Hz, 1H; NH).

Data for compound 11: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.32$ (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.88 (m, 1H), 7.63 (m, 2H), 7.51 (m, 1H), 7.39 (m, 2H), 7.11 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 6.97 (m, 1H), 6.58 ppm (m, 1H); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 163.77$, 158.40, 144.81, 142.68, 137.37, 135.37, 133.30, 129.74, 126.12, 124.95, 119.38 ppm; MS (CI): *m*/*z*: 301 [M^{+}+1]; elemental analysis calcd (%) for $\mathrm{C_{19}H_{12}N_2O_2}$ (300.3): C 75.99, H 4.03, N 9.33; found: C 75.86, H 4.30, N 9.11.

Data for compound 14: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.03$ (m, 4H), 7.47–7.28 (m, 8H), 6.62 (m, 4H), 5.63 (s, 2H; NH), 5.28 ppm (s, 2H; CH); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 153.45$, 137.03, 136.38, 128.86, 128.25, 127.20, 126.03, 112.60 ppm; MS (CI): *m*/*z*: 453 [M^{+}+1]; elemental analysis calcd (%) for $\mathrm{C_{26}H_{20}N_4O_4}$ (452.5): C 69.02, H 4.46, N 12.38; found: C 68.78, H 4.13, N 11.97.

Data for compound 17d: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.49$ (s, 1H), 8.01 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.79 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.54 (d, ^{3}J(H,H) = 8.6 Hz, 2H), 7.13 ppm (d, ^{3}J(H,H) = 8.6 Hz, 2H).

Data for compound 17e: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.41$ (s, 1H), 7.91 (m, 2H), 7.53 (d, ^{3}J(H,H) = 8.6 Hz, 2H), 7.18 (m, 2H), 7.09 ppm (d, ^{3}J(H,H) = 8.6 Hz, 2H).

Data for compound 17f: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 8.40$ (s, 1H), 7.78 (d, ^{3}J(H,H) = 8.4 Hz, 2H), 7.63 (d, ^{3}J(H,H) = 8.4 Hz, 2H), 7.52 (d, ^{3}J(H,H) = 8.6 Hz, 2H), 7.10 ppm (d, ^{3}J(H,H) = 8.6 Hz, 2H).

Kinetic measurements: The catalyst, the azide, and toluene were added in this order to a Schlenk flask under N_2. When required, benzene or a substituted toluene were added at this point. The flask was capped with a rubber septum and immediately placed in an oil bath preheated at 75 °C. The solution was stirred for one minute to dissolve all reagents and 0.2 mL was withdrawn for IR analysis. The consumption of the azide was followed by IR spectroscopy ($\nu_{N3} = 2120\ \mathrm{cm^{-1}}$) by withdrawing samples of the solution at regular times. Since all reactions were run in the presence of a large excess of toluene, the apparent first-order constants were fitted to the equation $-\mathrm{d}[\mathrm{ArN_3}]/\mathrm{d}t = k_{\mathrm{app}}[[\mathrm{Co(tpp)}]][\mathrm{ArN_3}]$. The concentration of [Co(tpp)] was calculated on the exact amount of catalyst weighed in each run and was considered to remain constant during the reaction.

Stoichiometric reaction of [Co(tpp)] with *p*-$\mathrm{O_2NC_6H_4N_3}$

^{1}H NMR analysis: [Co(tpp)] (10.3 mg, 1.5 10^{-2} mmol) and *p*-nitrophenylazide (2.7 mg, 1.5 10^{-2} mmol) were dissolved in $\mathrm{C_6D_6}$ (1 mL) at 60 °C. The consumption of the arylazide was monitored by recording an NMR spectrum every 5 min. New signals arose in the ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 60 °C) spectra at $\delta = 15.64$ (brs, 8H), 12.92 (brs, 8H), 9.56 (m, 12H), 7.82 (m, 4H), 7.41 (m, 4H). The ^{1}H NMR spectrum was identical to that of the product obtained by reaction of [Co(tpp)] (17.3 mg, 2.6 10^{-2} mmol) with *p*-nitrophenyldiazene (3.7 mg, 1.3 10^{-2} mmol) in $\mathrm{C_6D_6}$ (1 mL) at 60 °C.

UV/Vis analysis: The reaction mixture of [Co(tpp)] (100 mg, 0.15 mmol) and *p*-nitrophenylazide (25.7 mg, 0.16 mmol) in benzene (30 mL) was heated at 80 °C until complete consumption of the arylazide (UV/vis signal at 312 nm). A new signal at 344 nm was observed. Again the same signal is observed when [Co(tpp)] and *p*-nitrophenyldiazene are reacted with each other.

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