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Review

# Coordination chemistry of organic azides and amination reactions catalyzed by transition metal complexes

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## Contents

## Abstract

The interaction of organic azides with transition metal complexes will be discussed with particular attention to the coordination modes of these molecules. The stoichiometric reactions of organic azides with coordinated ligands will be considered and their use in amination reactions catalyzed by transition metal complexes will be discussed in detail. The utility of these catalytic reactions for the synthesis of organic compounds will be stressed.

*Keywords:* Organic azides; Transition metal complexes; Homogeneous catalysis; Organic synthesis; Amination reactions

## 1. Introduction

Organic azides are reactive molecules, which can be represented by the resonance formulas (A) and (B) (Fig. 1).

For the aromatic derivatives another resonance formula (C) can be considered although it goes against the Pauling's rule of charges present on vicinal atoms (Fig. 2).

These molecules are characterized by the lability of the $N_\alpha$–$N_\beta$ bond and, by thermal or photochemical activation, they readily lose dinitrogen, producing nitrene, "RN", species [1]. Resonance formulas (A) and (B) (Fig. 1) indicate a +1 charge on $N_\beta$ and −0.5 charge on $N_\alpha$ and $N_\gamma$ and a bond order 1.5 and

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Fig. 1. Resonance formulas for $RN_3$.

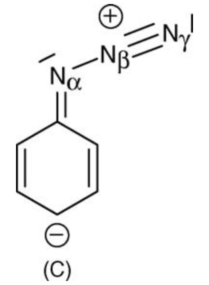


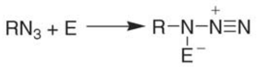
Fig. 2. Resonance formula for $ArN_3$.

2.5 for the bonds $N_\alpha–N_\beta$ and $N_\beta–N_\gamma$, respectively. These simplified data are in agreement with theoretical calculations and with the IR spectra, where the asymmetric stretching vibration of the azido group absorbs in the 2000–2135 $cm^{-1}$ region. The azido group is linear, and $N_\alpha$ can be considered $sp^2$ hybridized, carrying a lone pair. The azido group possesses all the qualities required to make it an excellent starting group for synthesis. The dipolar character and the relative instability of the azido group enable it to react in numerous fashions, depending on the structure of the molecule, the reagents and the conditions.

The most important reaction types of organic azides are indicated in Fig. 3 [1].

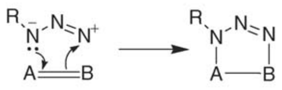
The above equations show the formation of primary intermediates, which in most cases react further and can yield a very large variety of products. Organic azides were in fact utilized for the synthesis of many types of open-chain and heterocyclic nitrogen-containing organic molecules. About thirty years ago, one of us wrote a review on the coordination chemistry of organic azides [2]. At that time, the interest was mainly focused on the function of these molecules as ideal reagents for synthesizing nitrene (or imido) complexes [3]. It was also supposed that in most cases the first step of the reaction sequences involved a labile coordination of the organic azide to the metal, followed by its reaction with an appropriate ligand previously bonded to the metal, with concomitant loss of dinitrogen (Scheme 1).

(a) Attacks by electrophilic reagents at the α-nitrogen atom



(b) Attacks by nucleophilic reagents at the azide terminus

(c) 1,3-Dipolar cycloaddition to polarophiles



(d) Decomposition reactions, resulting in the very reactive nitrenes

(e) Reductions

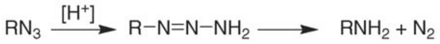
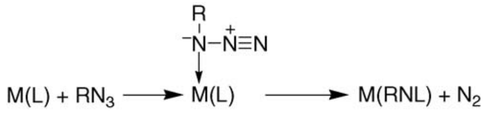


Fig. 3. The $RN_3$ reactivity [1].



Scheme 1.

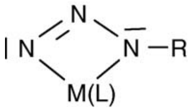


Fig. 4. The oxidative addition of $RN_3$ to M(L).

As the X-ray structures of metal complexes with an intact organic azide as ligand were unknown, coordination via the $N_\alpha$ atom seemed to be plausible. Another possible activation pathway involves an oxidative addition of the organic azide to the metal (Fig. 4).

In this review, which is not meant to be a comprehensive overview, inorganic azides such as $M(N_3)_6$ (M = Mo, W) [4], will not be discussed.

In the following, we will consider the stoichiometric reactions of organic azides with transition metal complexes, with an emphasis on the reactions relevant to catalytic transformations, which will be described in the last part of this review.

## 2. Stoichiometric reactions of organic azides with transition metal complexes

### *2.1. Complexes with the intact organic azide coordinated to the metal*

In Fig. 5, the structurally characterized metal–organo azide complexes are reported.

The reported structures include tantalum(V) complexes of $PhN_3$ and $p$-$Me_2NC_6H_4N_3$ **1** and **2** [5,6], a vanadium(V) adduct **3** containing $MesN_3$ (Mes = mesityl) [7], a mixed-metallic zirconium(IV)–iridium(III) complex **4** containing a bridging $PhN_3$ [8], palladium(II) **5** and copper(II) **6** adducts featuring a chelating 1-azido-2-pyrazolylcyclohexane ligand [9], copper(I) **7** and silver(I) **8** complexes with the azidoadamantane ligand [10] and a tungsten(VI) calixarene derivative of $PhN_3$ **9** [11].

The organic azide metal-adducts **1**–**4** and **9** have significantly bent N–N–N moieties and can be described as metal complexes of diazenimido ligands [5–7]. In contrast, the complexes **5**–**8** contain essentially linear N–N–N groups. The terminal, bent azido derivatives **1**–**3** lose dinitrogen under relatively

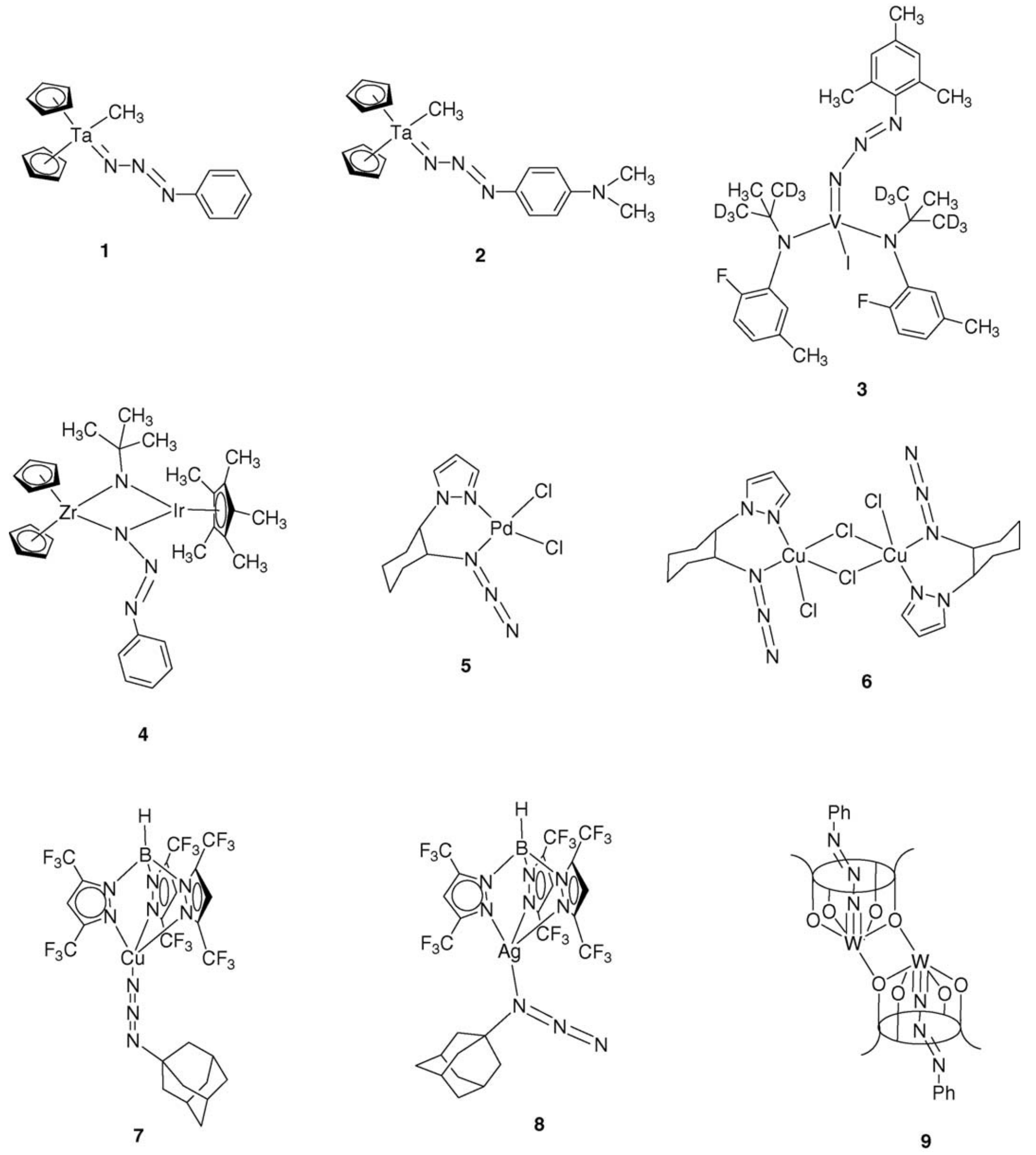


Fig. 5. Structurally characterized metal–organo azide complexes [5–11].

mild conditions, to yield metal–imido complexes. On the other hand, compound **9** does not decompose to the corresponding phenylimido derivative even upon heating. This has been attributed [11] to the fact that inside the calixarene cavity the intermediate formation of the metallatriazacyclobutene as required by the Bergman's mechanism for the extrusion of dinitrogen is not possible [6] (Fig. 4).

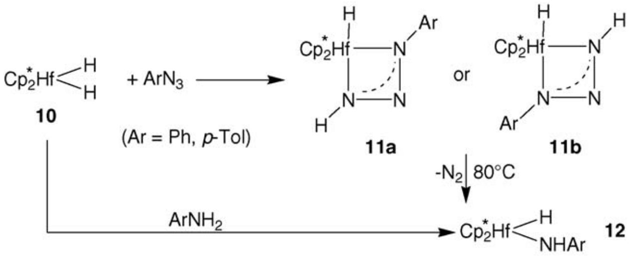
Compounds **5**–**8**, where the azido group is linear, are clearly divided in two groups. In the adducts **5**, **6** and **8** the coordination is at the $N_\alpha$ nitrogen of the organic azide, while in compound **7** the coordination is at the terminal $N_\gamma$ nitrogen. This has been attributed to the fact that copper(I) in **7** has enough π-donating ability to favor binding through the terminal nitrogen, while steric effects are not dominant in determining the binding preference (compare **7** and **8**) [10]. On the other hand, the coordination in **5** and **6** at $N_\alpha$ can be assisted by the chelation effect due to the nitrogen of the pyrazole substituent.

It has also been calculated that the intrinsic basicity of the terminal $N_\gamma$ and of the substituted nitrogen $N_\alpha$ favors $N_\alpha$. In $HN_3$, the proton affinity is $92.0\,kJ\,mol^{-1}$ greater for the substituted $N_\alpha$ nitrogen, but this trend applies to metals to a much lesser degree [10].

### 2.2. Stoichiometric reactions with coordinated ligands

#### 2.2.1. Reactions with metal hydrides

The most common products of the reactions of transition metal hydrides with organic azides are metal amido complexes, formally resulting from the insertion of the "RN" fragment of the organic azide into a metal–hydride bond. Typical examples include *trans*-$Pt(NHPh)Cl(PPh_3)_2$ from $PhN_3$ and $PtHCl(PPh_3)_2$ [12], $Re(NHC(O)Ph)(CO)_2(PPh_3)_2$ from benzoyl azide and $ReH(CO)_2(PPh_3)_3$ [13] and $Os_3H(\mu\text{-}NHTs)(CO)_{10}$ from toluene *p*-sulphonyl azide ($TsN_3$) and



Scheme 2. Ref. [18].

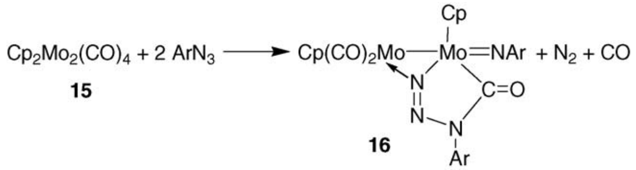
$Os_3H_2(CO)_{10}$ [14]. The isolation of the monosubstituted triazenido complexes $W(NO)(NHNN$*p*-Tol$)(CO)(PPh_3)_2$ and $Re(NHNN$*p*-Tol$)(CO)_2(PPh_3)_2$ from the reactions of *p*-tolyl azide with $WH(NO)(CO)_2(PPh_3)_2$ and $ReH(CO)_2(PPh_3)_3$, respectively [15], and of $Os_3H(NHNNPh)(CO)_{10}$ from the reactions of $Os_3H_2(CO)_{10}$ and $PhN_3$ [16], suggested triazenido complexes might be reactive intermediates in the formation of amides from organic azides and metal hydrides. It is known that free phenyltriazene, PhN=N–NH$_2$, decomposes above −20 °C to give aniline and dinitrogen quantitatively [17], an observation compatible with the suggestion that triazenido complexes might be unstable with respect to dinitrogen loss and formation of metal amido species. Moreover, $Os_3H(NHNNPh)(CO)_{10}$ decomposes upon thermolysis with extrusion of dinitrogen to give $Os_3H_2(CO)_9(\mu_3\text{-NPh})$ [16]. This hypothesis has been fully confirmed by the results obtained by Bercaw [18]. It has been shown that $Cp^*{}_2HfH_2$ **10** ($Cp^* = \eta^5$-1,2,3,4,5,-pentamethylcyclopentadienyl) smoothly reacts with $ArN_3$ (Ar = Ph, *p*-tolyl) to afford moderately stable triazenido complexes of hafnium, $Cp^*{}_2HfH(NHNNAr)$ **11**. These compounds, upon thermolysis at 80 °C, lose dinitrogen to form hafnium arylamido complexes, $Cp^*{}_2HfH(NHAr)$ **12**, which can alternatively be prepared from $ArNH_2$ and $Cp^*{}_2HfH_2$ **10**. Labeling studies with $Ph^{15}NNN$ and $PhN^{15}NN$ have shown that it is the γ-nitrogen atom of the organic azide to formally insert into a hafnium–hydride bond (Scheme 2).

### 2.2.2. Reactions with metal carbonyls

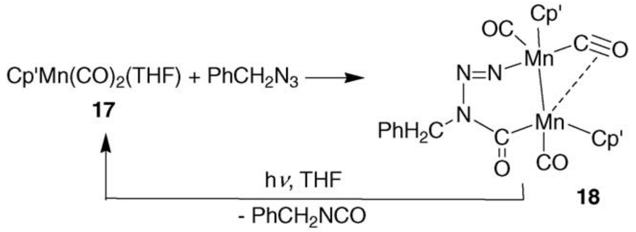
The reactions of aryl and aroyl azides, $ArCON_3$ (Ar = Ph, *p*-Tol) with *trans*-$IrX(CO)(PR_3)_2$ **13** and $RhX(CO)(PR_3)_2$ **14** (X = Cl, Br, I) have been studied mainly in the aim of obtaining dinitrogen complexes [19]. As a matter of fact, the isocyanates corresponding to the employed organic azides were also formed. Spectral and kinetic evidence supports the mechanism depicted in Scheme 3.

In the presence of an alcohol, the isocyanate is transformed into the corresponding carbamate, whereas, when it is absent, the isocyanate displaces dinitrogen from the final metal complex. Even carbon monoxide displaces dinitrogen and thus the reaction can be made catalytic. The effects of changing the nature of the organic azide, the central metal and the ancillary ligands on the reaction rate have been examined. The obtained results suggest that the organic azide functions as an electrophile and the metal as a base in a reaction related to an oxidative addition. The observed rate law is: $-d[IrCl(CO)(PR_3)_2]/dt = k[IrCl(CO)(PR_3)_2][R'N_3]$. Electron-withdrawing substituents on the organic azide accelerate the reaction, as shown by the increasing rates: *p*-azido toluene < phenyl azide < furoyl azide. Reactions of the complexes containing alkyl phosphines as ligands are considerably faster than those of the corresponding triphenylphosphine complexes, and the halogens favor the reaction in the order: I > Br > Cl, that is with the same reactivity sequence observed in the addition of $H_2$ and $O_2$ to the iridium complex [20]. The most important aspect of the mechanism depicted in Scheme 3, is that the organic azide attacks the metal and not a coordinated ligand and then collapses to form the dinitrogen complex and the aryl isocyanate. However, reaction of $Cp_2Mo_2(CO)_4$ **15** ($Cp = \eta^5$-cyclopentadienyl), where a molybdenum–molybdenum triple bond is present, with aryl azides gives a metallacycle **16** in which the organic azide has acted as a nucleophile towards a carbon monoxide ligand (Scheme 4) [21].

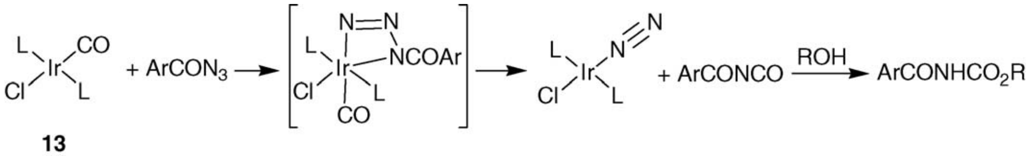
The X-ray structure of the derivative with Ar = *p*-$Bu^tC_6H_4$ has been solved. The mechanism by which the metallacycle is formed remains to be clarified. Similarly, the reaction of benzyl azide with $Cp'Mn(CO)_2(THF)$ **17** ($Cp' = \eta^5$-$CH_3C_5H_4$) results in the formation of a metallacycle **18** in which a carbon monoxide ligand has been incorporated (Scheme 5) [22].



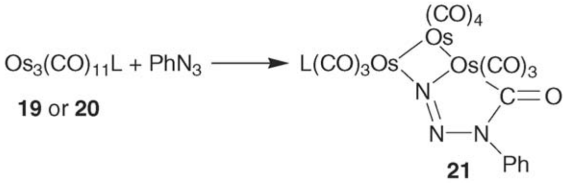
Scheme 4. Ref. [21].



Scheme 5. Ref. [22].



Scheme 3. Ref. [19].



Scheme 6. Ref. [23].

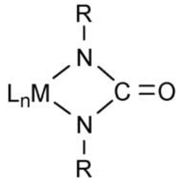


Fig. 6. General structure of ureylene complexes [2].

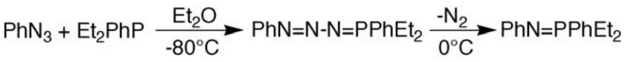
The metallacycle **18**, whose X-ray structure has been clarified, loses $PhCH_2NCO$ when irradiated in THF solution. The extra carbon monoxide necessary in this reaction must come from decomposition of the starting complex. The identity of the intermediate leading to the dinuclear complex shown in Scheme 5 (a mononuclear derivative where the organic azide has displaced THF or has attached carbon monoxide) has not been clarified. The reactive metallacycle can be stabilized by bridging of the terminal nitrogen between two metals, as evidenced by the complex **16** reported in Scheme 4, and by the complexes of general structure **21** obtained by reaction of $PhN_3$ with $Os_3(CO)_{11}(NCMe)$ **19** and $Os_3(CO)_{11}(NC_5H_5)$ **20** (Scheme 6) [23].

Note that in the metallacycles **21** reported above, the α-nitrogen of the organic azide is always the one involved in the nucleophilic attack to carbon monoxide, while with metal hydrides complexes the nitrogen involved was the one in the γ-position [18]. This might reflect the greater nucleophilicity and proton affinity of $N_\alpha$ with respect to $N_\gamma$ [10]. The reactions of organic azides with transition metal carbonyl derivatives can also lead to ureylene complexes (Fig. 6) [2], but these derivatives will not be considered here.

### 2.2.3. *Reactions with metal phosphine complexes*

The reactions of aromatic azides with trivalent phosphorus compounds were first studied by Staudinger and co-workers [24]. The initial product is an unstable 1:1 adduct, which in some cases could be isolated by low temperature work-up. One example is reported in Scheme 7.

The phosphazide $PhN{=}N{-}N{=}PPhEt_2$ was isolated at low temperature, but in solution at 0 °C dinitrogen was evolved and the phosphimine $PhN{=}PPhEt_2$ was produced. The kinetics of the reaction of substituted aryl azides with triarylphosphines was studied and it has been found that the rate was accelerated by electron-withdrawing substituents and retarded by electron-donating groups. A careful study of the Staudinger reaction of aryl azides has shown that adherence to second order kinetics is only approximate. Deviations increased when electron-releasing substituents were present on the triarylphosphine and electron-withdrawing substituents on the aryl azide. Evidence was presented for a reaction proceeding through two isomeric transition states. The first (A) involves the attack of the phosphine at the terminal nitrogen of the organic azide, whereas in the second transition state (B) the phosphorus is at least partially bonded to the α nitrogen atom (Fig. 7).



Scheme 7. Ref. [24].

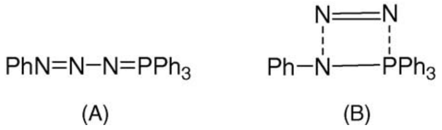


Fig. 7. The transition states for the reaction of $PhN_3$ with $PPh_3$ [24].

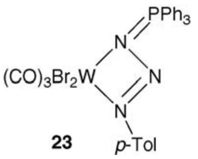


Fig. 8. Structure of $WBr_2(CO)_3(p\text{-}TolN_3PPh_3)$ [15–25].

Note that the intermediate (B) is related to the intermediates formed in the reactions of organic azides with transition metal carbonyl complexes discussed above.

In view of the reactions between organic azides and phosphines, it is not surprising that in the reactions of organic azides with complexes having phosphines as ligands, the corresponding phosphimine adducts are readily formed with the phosphine liberated from the metal. Moreover, phosphazide complexes have also been isolated. *p*-Tolyl azide reacts with $WBr_2(CO)_3(PPh_3)_2$ **22** to form the complex **23** reported in Eq. (1) [15]:

$$\underset{\mathbf{22}}{WBr_2(CO)_3(PPh_3)_2} + p\text{-}TolN_3 \rightarrow \underset{\mathbf{23}}{WBr_2(CO)_3(p\text{-}TolN_3PPh_3)} \tag{1}$$

The seven coordinated tungsten complex **23** was characterized by X-ray diffraction studies: the phosphazide ligand is bonded to the metal fragment in a bidentate fashion, through the α and γ nitrogen atoms [25] (Fig. 8).

More recently, a cyclic (*Z*)-phosphazide was found to act as a monodentate two-electron donor through the less sterically hindered β-nitrogen atom [26] (Fig. 9).

It has also been discovered that α-zirconated phosphine **24** allows the synthesis of phosphazides derivatives by reaction with organic azides. The reaction involves a formal [1 + 3] cycloaddition that occurs exclusively with the γ-nitrogen atom of the

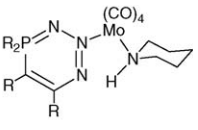
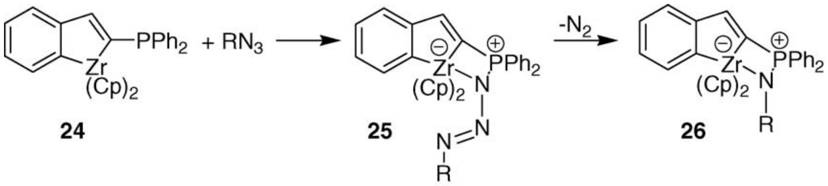


Fig. 9. β-Nitrogen coordination of (*Z*)-phosphazide to molybdenum [26].



Scheme 8. Ref. [27].

organic azide, to afford zwitterionic complexes **25** (Scheme 8) [27].

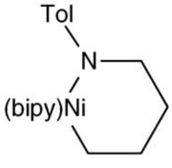
Decomposition of these complexes occurs with loss of dinitrogen, leading to other new polycyclic zwitterionic species **26**. Finally, the phosphine complexes $Co(PR_3)_2X_2$ (X = Cl, Br; R = Et, Ph, Cy), react with furoyl azide ($FurN_3$) at 25 °C to give the phosphimine derivatives $Co(FurN{=}PR_3)_2X_2$ [28]. At lower temperatures the intermediate complex $Co(FurN_3PCy_3)Br_2$ with the phosphatriazene as ligand could be isolated.

In view of the reactions of organic azides with ligands such as CO and $PR_3$ coordinated to the metal, it is not surprising that addition to metal coordinated isocyanides also takes place [29]. The 1,3-dipolar cycloaddition of $PhN_3$ to $Tp'Rh(CNR)_2$ (Tp′ = hydrido-tris(3,5-dimethylpyrazolyl)borate) or to $Cp^*Rh(CNR)_2$, produces the complexes $Tp'Rh(CNR)(\eta^2\text{-}PhN{=}C{=}NR)$ and $Cp^*Rh(CNR)(\eta^2\text{-}PhN{=}C{=}NR)$.

### 2.2.4. *Reactions with single metal–carbon bonds*

Insertion of organic azides into the metal–carbon bond has also been observed. The reaction of $PhN_3$ with $Cp_2ZrR_2$ (R = Me, Ph) gives the 1,3-triazenido complexes $Cp_2ZrR(RNNNPh)$, while *mer*-$CoMe_3(PMe_3)_3$ and *p*-$TolN_3$ react to give $CoMe_2(MeNNN$*p*$\text{-}Tol)(PMe_3)_2$ [30]. In all three cases the triazenido group appears to be bidentate. The terminal nitrogen atom of $PhN_3$ inserts into one of the carbon–zirconium bond of zirconacyclopentane **27** to give a novel 18 electron azazirconacycle **29**, that is very stable toward hydrolysis (Scheme 9) [31].

An X-ray diffraction study has been carried out on the triazenido alkyl zirconocene complex **29**. The supposed intermediate **28** with the organic azide bonded to the metal via the γ-nitrogen atom in a linear fashion could not be isolated nor characterized in solution.

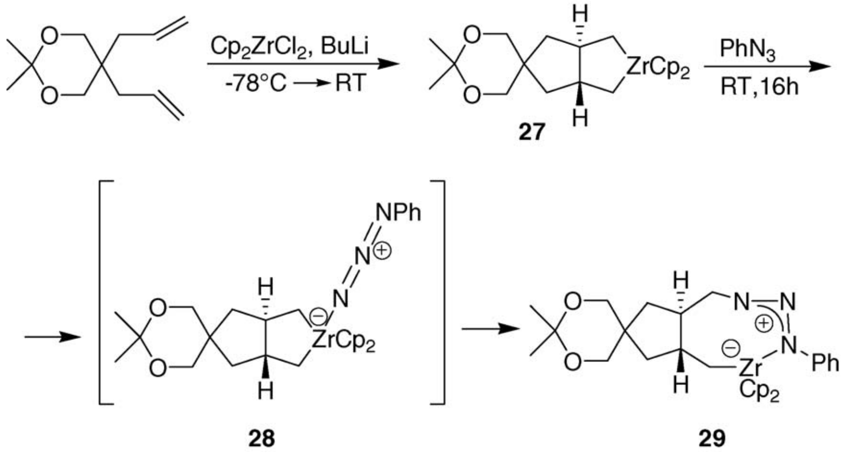


**30**

Fig. 10. Structure of Ni(bipy){N-κ*N*(*p*-Tol)$(CH_2)_4$-κ*C*} **30** [32a].

THF solutions of $Ni(bipy)R_2$ (R = Me, Et; bipy = 2,2′-bipyridine) react cleanly with *p*-$TolN_3$ to give dinitrogen and the nickel(II) amido complexes Ni(bipy){N(*p*-Tol)(R)}R in excellent yields [32a]. Experiments conducted with $N{=}N{=}^{15}NPh$ have demonstrated that the N–C bond of the organic azide is maintained during the formal insertion into the nickel–alkyl bond to give the Ni–N(*p*-Tol)(R) product. The reaction is not limited to acyclic nickel dialkyls, and the nickelacyclopentane complex $Ni(bipy)(CH_2)_4\text{-}\kappa^2C$ undergoes reaction with *p*-$TolN_3$ to give the corresponding cyclic nickel amido derivative Ni(bipy){N-κ*N*(*p*-Tol)$(CH_2)_4$-κ*C*} **30** (Fig. 10).

No intermediates have been observed in these reactions. The room temperature reaction of $(PMe_3)_2Ni(2\text{-}(CH_2CMe_2\text{-}\kappa C)C_6H_4\text{-}\kappa C^1)$ with *p*-$TolN_3$ results in evolution of dinitrogen and a clean formation of *N*-*p*-tolyl-3,3-dimethyl-2,3-dihydro-1*H*-indoline [32b]. The reaction probably proceeds by insertion of a “*p*-TolN” fragment from *p*-$TolN_3$ into the Ni–C(aryl) bond to give an intermediate azametallacycle $L_nNi(N\text{-}\kappa N(p\text{-}Tol)(2\text{-}(CH_2CMe_2)C_6H_4\text{-}\kappa C^1)$, which then undergoes C,N reductive elimination to afford the indoline.



Scheme 9. Ref. [31].

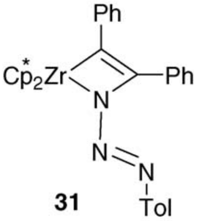
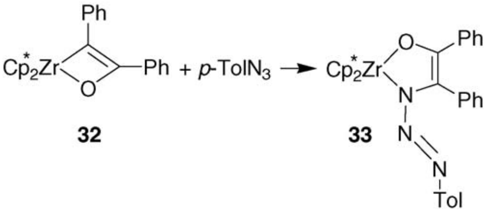


Fig. 11. The azacyclobutene insertion product **31** [33].



Scheme 10. Ref. [33].

The zirconium diphenylacetylene complex $Cp^{*}{}_2Zr(C_2Ph_2)$ reacts with $p$-$TolN_3$ to give the azacyclobutene insertion product **31** whose structure has been confirmed by X-ray analysis [33] (Fig. 11).

This compound is not prone to lose dinitrogen by thermal activation. Similarly, the complex **32** obtained by reaction of $Cp^{*}{}_2Zr(C_2Ph_2)$ with $N_2O$, which is unstable to loss of dinitrogen, reacts with $p$-$TolN_3$ to give a five-membered azametallacycle **33** [33] (Scheme 10).

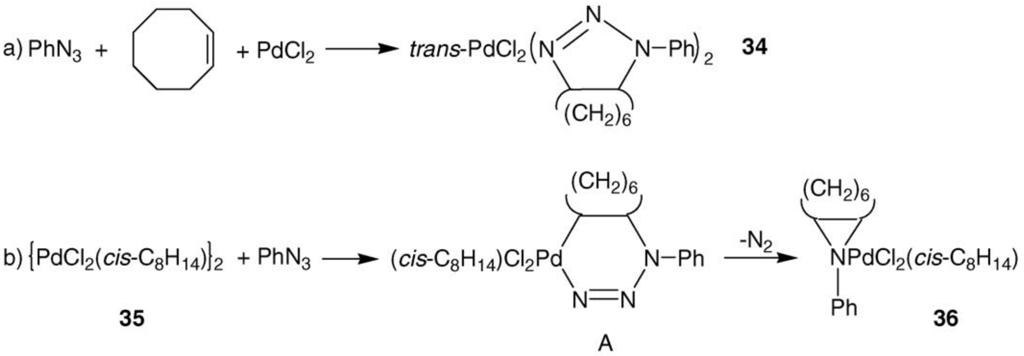
Surprisingly, until now, few investigations had been devoted to the reactions of organic azides with transition metal olefin complexes (or viceversa), probably because organic azides and unsaturated hydrocarbons react without the assistance of the metal [1]. However, as we will see in the paragraph devoted to the catalytic reactions (Section 3.2), transition metal catalysts can markedly influence the rate and the outcome of these reactions.

Reaction of $PhN_3$ with alkenes in the presence of $AlCl_3$ gives an aziridinium–$AlCl_3$ complex via an organic azide–$AlCl_3$ adduct. This reaction is followed by ring opening reactions of the aziridinium–$AlCl_3$ complex to give *N*-allyl anilines and/or *N*-phenyl-β-chloramines after work-up with aqueous $Na_2CO_3$. However, by reaction with *cis*-cyclooctene a novel (for that time) aziridine, 9-phenyl-9-azabicyclo[6.1.0]nonane, was obtained after the work-up [34a].

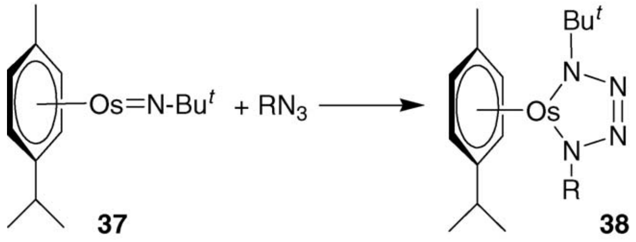
We mention only briefly that decomposition of 2-azidodiphenylenethane and 2-azidobiphenyl in the presence of $AlCl_3$ gave 9,10-dihydroacridine and carbazole, respectively [34b], and that reaction of $BCl_3$ with an *ortho*-aryl and *ortho*-diazoaryl phenyl azides at room temperature yield fused azoles via 1,5-cyclization of a probable singlet nitrenium ion intermediate [34c].

By reaction at 70 °C of $PhN_3$ with a suspension of $PdCl_2$ in *cis*-cyclooctene, the complex $PdCl_2(triazoline)_2(CHCl_3)_2$ **34** was isolated and its crystal and molecular structure determined [35]. Preformed $\{PdCl_2(cis\text{-}C_8H_{14})\}_2$ **35** reacts with $PhN_3$ in cyclooctene at 70 °C to give a $PdCl_2(aziridine)_2$ complex **36** (Scheme 11). The triazoline complex **34** proved to be rather stable and it decomposed only upon reflux in toluene, to give palladium metal and a complex mixture of organic products. When the complex **34** was heated under dinitrogen at 70 °C in cyclooctene for 6 h, and then left to cool overnight, no reaction was observed, which means that the triazoline complex is not an intermediate leading to the aziridine derivative by loss of dinitrogen, a reaction that is observed in the organic chemistry of triazolines which readily give the corresponding aziridines. Compound **35** does not manifest any catalytic activity in the reaction between $PhN_3$ and *cis*-$C_8H_{14}$. These results seem to suggest that when uncomplexed palladium(II) chloride is present in the reaction medium it rapidly coordinates the triazoline slowly formed outside the coordination sphere of the metal. At least in this case the triazoline loses dinitrogen and rearranges to the corresponding *N*-*cyclo*-octylidene-aniline, $PhN{=}C(CH_2)_7$. On the other hand, when a preformed palladium–olefin complex **35** is present, the triazoline is not able to displace the olefin from the metal and the preferred reaction is the attack of the organic azide on the coordinated olefin, possibly via the intermediate (A) which by subsequent loss of dinitrogen gives the final aziridine complex **36** (Scheme 11).

This finds some support from the isolation of metallacycles derivatives, obtained by attack of organic azides on coordinated carbon monoxide as discussed above. Other attempts at that time to find transition metal complexes able to catalyze the reaction of $PhN_3$ with olefins were unsuccessful. Derivatives such as $\{RhCl(olefin)_2\}_2$ decomposed during the reaction. Very



Scheme 11. Ref. [35].



Scheme 12. Ref. [37].

recently it has been reported that reaction of TsN$_3$ and a silane with unactivated olefins, catalyzed by a cobalt(II)–Schiff base complex, results in a hydrozidation reaction, giving alkyl azides with Markovnikov selectivity [36]. This is an important reaction, which has no precedent in the literature.

### 2.2.5. Reactions with metal–imido and metal–carbene complexes

[3 + 2] Cycloaddition reactions of organic azides to an osmium imido complex **37** generating a series of tetra-azametallacyclopentene complexes **38** have been reported (Scheme 12) [37].

In the main group, the reaction of Me$_2$Si(Bu$^t$N)$_2$Ge **39** with $p$-TolN$_3$ also probably proceeds via an imido intermediate A (Scheme 13) [38].

The intermediacy of transient imido species A has also been proposed in the formation of other tetrazene complexes [39].

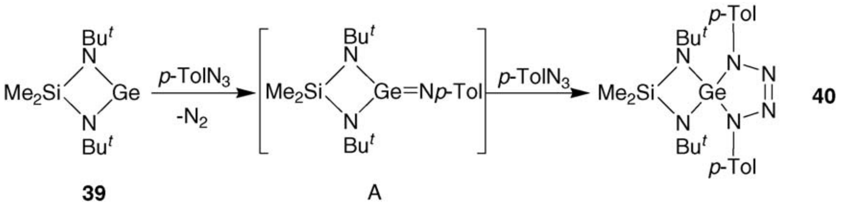
Addition of Bu$^t$N$_3$ or ArN$_3$ (Ar = Ph, $p$-Tol) to a benzene solution of Cp$_2$Zr(=NBu$^t$)(THF) **41** gave the corresponding [2 + 3] cycloaddition products **42** (Scheme 14) [40].

At slightly elevated temperatures (45 °C) the aryl-Bu$^t$ tetrazene derivative **43** underwent loss of organoazide (Bu$^t$N$_3$) and in the presence of ArN$_3$ the bis-aryl tetrazene **44** derivative was obtained. In the absence of free organic azide the reactions led to (Cp$_2$ZrNAr)$_2$. In an effort to trap the intermediate Cp$_2$Zr=NAr **45**, reactions were conducted in the presence of strained alkenes, imines and alkynes (Schemes 15 and 16) [40].

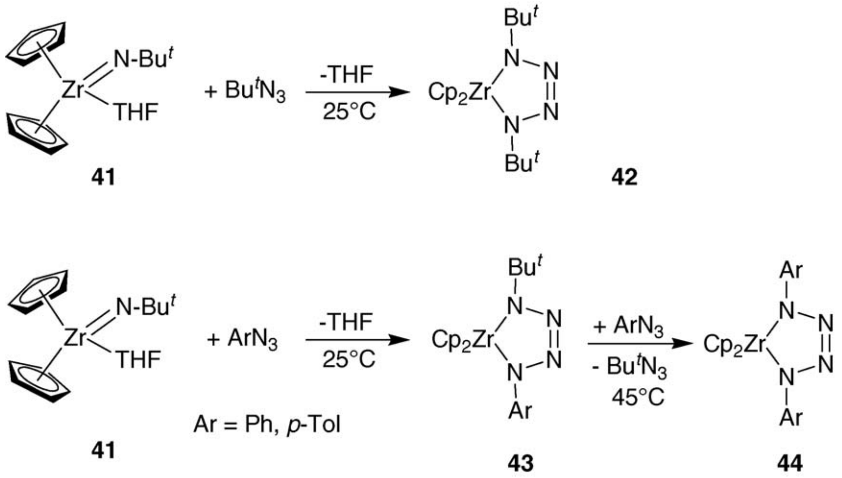
The reactions were successful and an X-ray structural determination was carried out on the unusual seven membered metallacycle **46**b obtained in the presence of alkynes (Scheme 15).

Cycloaddition of organic azides to a metal–nitrene bond to give tetrazene derivatives, was also observed by reaction of ArN$_3$ (Ar = Ph, mesityl) with Ir(Mes)$_3$ [41]. Very recently, a tetra-azazirconacycle complex was obtained by reaction of $p$-TolN$_3$ with Zr[$o$-(Me$_3$SiN)$_2$C$_6$H$_4$]$_2$ [42].

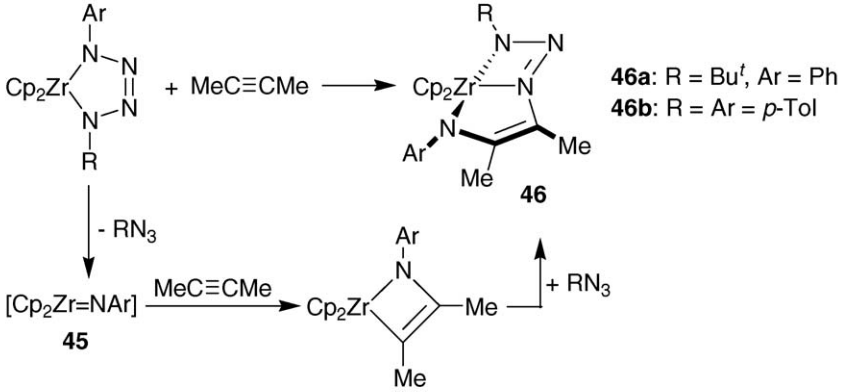
Few reports have appeared on the reactions of metal–carbene complexes with organic azides. The pentacarbonyl (diphenylcarbene) complexes (CO)$_5$M=CPh$_2$ (M = Cr, W) react with trimethylsilyl azide, Me$_3$SiN$_3$, to afford benzophenoneimine(pentacarbonyl)–chromium and tungsten complexes (CO)$_5$M(N(H)=CPh$_2$), with evolution of dinitrogen [43]. The carbene–tungsten complex reacts with Bu$^n$N$_3$ to give (CO)$_5$W(N(Bu)=CPh$_2$). These reactions correspond to a formal insertion of the "NR" fragment into the metal–carbene bond. Imido insertion into a cobalt–carbene bond via an unusual terminal cobalt(III)–imido complex, has been recently reported by reaction of ArN$_3$ (Ar = $p$-MeC$_6$H$_4$, $p$-OMeC$_6$H$_4$) with a Co(I) tris(carbene) complex [44]. In a somewhat related reaction, the complexes CpRh(=C=CHR)PPr$^i_3$ **47** react with



Scheme 13. Ref. [38].



Scheme 14. Ref. [40].



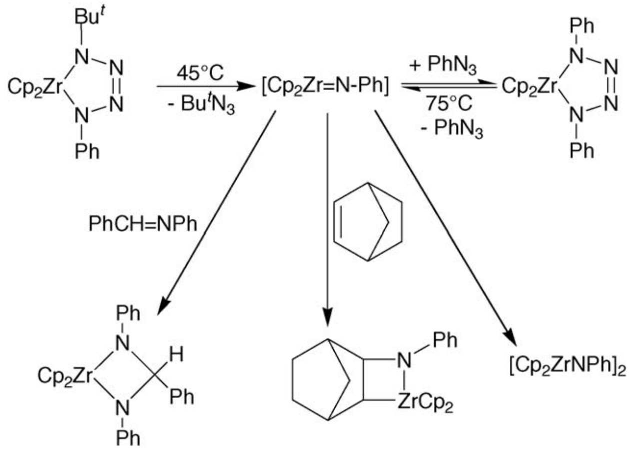
Scheme 15. Ref. [40].

benzoyl azide to produce the metallacycles **48** reported in Scheme 17 [45].

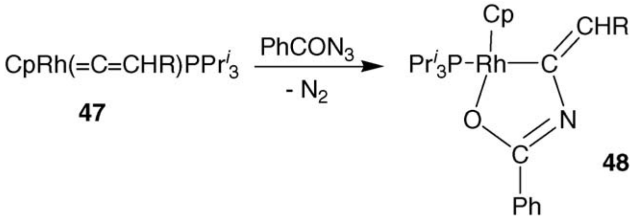
By reaction with $PhN_3$ (R = Ph), the keteneimine complex CpRh(PhN=C=CHPh)($\eta$*N*,$C^1$)PPri$_3$ was obtained.

Reactions of carbodiimides with $TsN_3$ in the presence of copper powder afforded guanidines (Scheme 18) [46].

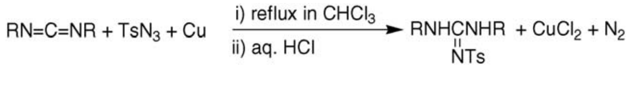
Reactions with pentacarbonyl iron instead of copper powder also gave the guanidines. These reactions are thought to proceed by initial formation of an organic azide–metal complex and/or a nitrene–metal intermediate, followed by insertion of the carbodiimides into a metal–nitrogen bond.



Scheme 16. Ref. [40].



Scheme 17. Ref. [45].



$$RN{=}C{=}NR + TsN_3 + Cu \xrightarrow[\text{ii) aq. HCl}]{\text{i) reflux in } CHCl_3} RNH\underset{NTs}{\underset{\|}{C}}NHR + CuCl_2 + N_2$$

Scheme 18. Ref. [46].

In view of the notable number of imido and carbene complexes of transition metals now known, many different reactions with organic azides are to be expected.

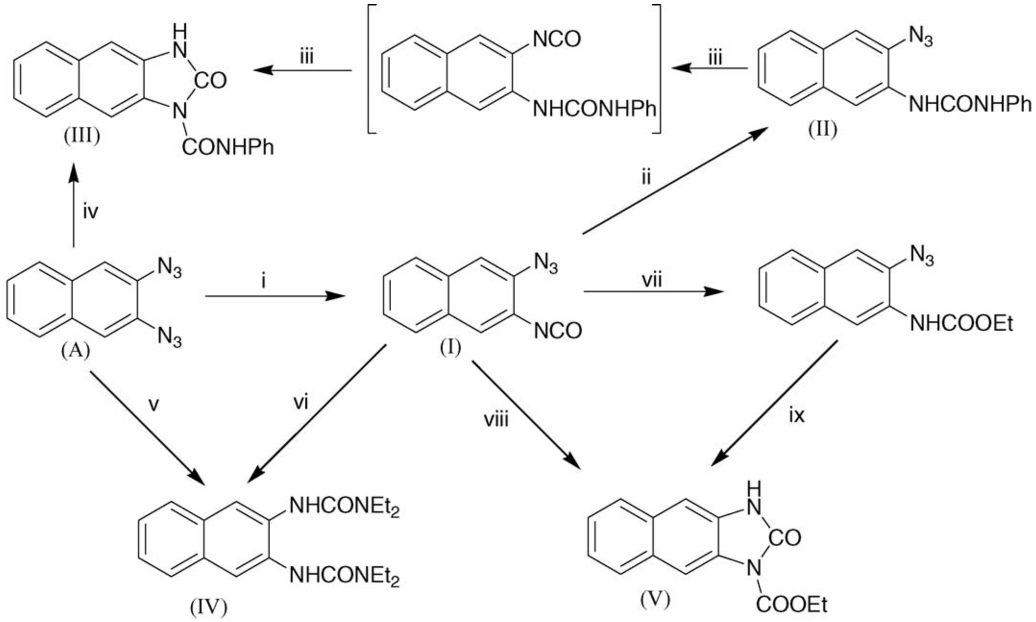
## 3. Reactions of organic azides catalyzed by transition metal complexes

### 3.1. Reactions with carbon monoxide

Although Collmann stated that in the absence of a metal complex, CO and organic azides do not react at a measurable rate [19], people have attempted the direct synthesis of isocyanates from aromatic azides and uncomplexed CO in an uncatalyzed reaction [47,48]. However, reaction conditions were rather harsh and the selectivity was rather poor. With $PhN_3$, only at CO pressure above 136 atm and at 160–180 °C phenyl isocyanate was obtained, with only a trace of azobenzene [47]. In the absence of a solvent, the reaction is more complex and 1,3-diphenylurea and aniline were the products [48]. By using Freon 113 (1,1,2-trichloro-1,2,2,-trifluoroethane) as a solvent that does not contain hydrogen, a study was carried out on the influence of the substituents on the aromatic azides [48]. It was found that substituents with positive mesomeric effect in *para* with respect to the azido group increase the reaction rate and the selectivity in the formation of the isocyanate in the order: $OCH_3 > CH_3 > Cl > H$. The beneficial influence of electron donor substituents has been attributed to the stabilization of an intermediate nitrene radical, “ArN”, supposed to be formed by initial dinitrogen loss from the organic azide. In one paper [47], the reactions were carried out in stainless steel, tantalum-lined or glass-lined autoclaves, and thus adventitious catalysis by the metal of the autoclave can be ruled out.

Several groups VIII–X metal carbonyls catalyze the decomposition of aryl azides to yield in the presence of CO and a low concentration of hydrogen, the corresponding symmetrical disubstituted ureas (Eq. (2)) [49]:

$$2ArN_3 + CO + H_2 \xrightarrow{M_x(CO)_y} ArNHCONHAr + 2N_2 \tag{2}$$



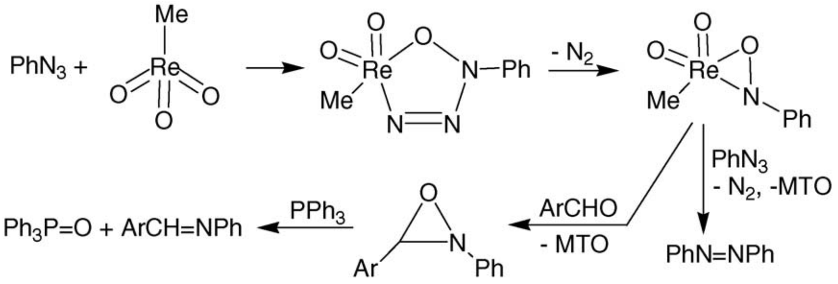
Scheme 19. (i) Homogeneous catalyst (hc) or supported catalyst (sc), CO; (ii) $PhNH_2$; (iii) CO, hc; (iv) CO, $PhNH_2$, hc; (v) CO, $Et_2NH$, hc; (vi) CO, $Et_2NH$, hc; (vii) EtOH; (viii) CO, EtOH, hc; (ix) CO, EtOH, hc [52].

The formation of intermediate nitrenoid species has been proposed. A kinetic study has been carried out on the reaction of $ArN_3$ with CO at atmospheric pressure and 50 °C [50a]. The catalysts used were $MX(CO)(PR_3)_2$ (M = Rh, Ir; X = F, Cl, Br; R = Ph, OPh, Cy, *p*-$ClC_6H_4$, *p*-$MeOC_6H_4$, $Bu^n$). The reaction rate, $r = k[ArN_3][MX(CO)(PR_3)_2]$, is greatly accelerated by electron-withdrawing substituents on the *para* position of the organic azide, a result which is opposite to what observed in the reactions carried out in the absence of the metal (see above). More basic ligands on the complex also accelerate the reaction. The 1:1 adduct between the organic azide and the catalyst has not been detected. A kinetic study has also been carried out on the formation of *p*-carboethoxyphenyl isocyanate from *p*-ethyloxycarbonylphenyl azide and CO, in the presence of supported rhodium complexes, synthesized by reaction of $RhCl(CO)(Ph_2PCH_2CH_2Si(OEt)_3)_2$ with porous silica glasses [50b]. The anchored complexes are catalytically 500–1000 times less active than the homogeneously dissolved one. Their activity decreases with increasing metal loading of the glasses. The activation energy of the heterogeneous reaction is greater than that of the homogeneous reaction, and the reaction rate is independent of the pellet diameter, the pore volume, the pore diameter and the specific surface of the glass support, which indicate that a retardation of the reaction by pore diffusion is not involved.

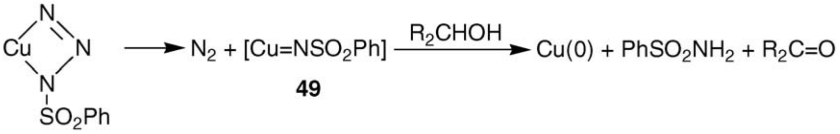
The catalytic activity of rhodium(I) complexes even with chelating diphosphines as ligands, in the carbonylation reaction of aromatic azides *p*-$RC_6H_4N_3$ (R = H, $NO_2$) at atmospheric pressure and 25–80 °C, leading to the corresponding isocyanates has been studied [51]. $[Rh(DPPE)_2]Cl$ (DPPE = $Ph_2PCH_2CH_2PPh_2$), $[Rh(DPPP)_2]Cl$ (DPPP = $Ph_2PCH_2CH_2CH_2PPh_2$), $Rh(Cl)(CO)(PPh_3)_2$ and $[Rh(DPPP)(CO)Cl]_2$ are the most active catalysts, and maintain their high activity even in the presence of *p*-$R'C_6H_4NH_2$, which gives the corresponding ureas, *p*-$RC_6H_4NHCONHC_6H_4R'$-*p*, or ethanol, which gives the carbamate *p*-$RC_6H_4NHCO_2Et$. The selectivity in isocyanate was excellent (>98% in most cases), and *p*-$NO_2C_6H_4N_3$ reacted faster than unsubstituted phenyl azide. $RhCl(CO)(PPh_3)_2$ has been heterogenized by reaction with a polymeric phosphine. Its activity in the catalytic carbonylation of aromatic azides was found to be comparable to that of the homogeneous system [51b]. The heterogenized catalyst can be recycled without any decrease in its catalytic activity. By carbonylation at atmospheric pressure and 45 °C of 2,3-diazido naphthalene (A) catalyzed by $[Rh(DPP)(CO)Cl]_2$ or by $RhCl(CO)(PPh_3)_2$ heterogenized with a polymeric phosphine, 2-azido-3-isocyanato naphthalene(I) has been obtained (Scheme 19) [52].

Compound (I) reacted with aniline to give *N*-phenyl-$N^1$[2(3-azido)naphthyl]urea(II), which in the presence of CO and of the homogeneous catalyst $[Rh(DPPP)(CO)Cl]_2$ gave 1-phenylaminocarbonyl-1*H*-2,3-dihydronaphth[2,3-d]imidazolin-2-one(III). Compound (III) was also obtained by the direct catalytic carbonylation of (A) carried out in the presence of aniline. The reaction of (I) with CO in the presence of the homogeneous catalyst did not allow the isolation of any heterocyclic product when diethylamine was used, 2,3-*N*,*N*-diethylureidonaphthalene(IV) being formed. The catalytic carbonylation of (I) in the presence of ethanol gave 1-ethoxycarbonyl-1*H*-2,3-dihydronaphth-[2,3-d]imidazolin-2-one(V). The results reported here confirm the usefulness of rhodium(I) catalysts in the carbonylation of aromatic azides, allowing the selective synthesis under mild conditions of organic products that appear to be difficult to prepare by conventional routes.

We briefly mention here a peculiar reaction of organic azides with aromatic aldehydes [53]. The reaction produces imines in good yields when a stoichiometric quantity of



Scheme 20. Ref. [53].



Scheme 21. Ref. [55].

triphenylphosphine is added, along with a catalytic amount of methylrhenium trioxide (MTO) (Eq. (3)):

$$RN_3 + ArCHO + PPh_3 \xrightarrow{MTO} ArCH{=}N{-}R + N_2 + PPh_3O$$

$$(R = Ph, Bu^n, n\text{-hexyl}) \qquad (3)$$

These reactions occur even in the absence of MTO, but more slowly. Phenyl azide is catalytically decomposed under mild conditions by trace of MTO in dry benzene, to give azobenzene PhN=NPh. The proposed reaction mechanism is reported in Scheme 20.

What is surprising in this reaction is that the organic azide apparently does not react with free phosphine, an easy reaction discussed previously.

### 3.2. Reactions with unsaturated hydrocarbons

Copper is known to be an effective catalyst for the decomposition of diazoalkanes and diazocarbonyl compounds. An intermediate copper–carbene complex was postulated [54]. Copper is also a good catalyst for the decomposition of benzenesulphonyl azide [55]. Cuprous chloride was even more effective, but cuprous oxide was inert [56]. In refluxing alcohols the main product was benzenesulphonamide, with dinitrogen evolution. An intermediate copper–nitrene complex **49** was supposed (Scheme 21).

However, it has been said that the decomposition of the organic azide was accompanied by the oxidation of a considerable part of the copper catalyst. In a succeeding article, Kwart and Khan investigated the copper catalyzed decomposition of benzenesulphonyl azide in cyclohexene [57]. A variety of products were formed, mainly benzenesulphonamide, the aziridine from the addition of the nitrene fragment to the double bond, an enamine and cyclohexanone (Scheme 22).

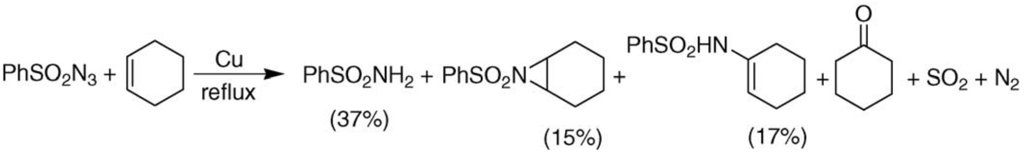
Here too, the authors invoked the formation of a copper–organic azide complex, which evolves to a copper–nitrene derivative. However, a copper catalyzed radical reaction seemed also to be a reasonable hypothesis [56].

Azidoformate reacts with allylic ethers to give 1-alkoxy-1-(alkoxycarbonylimino)alkane under catalysis by $PdCl_2(PhCN)_2$ (Eq. (4)) [58]:

$$CH_2{=}CH{-}CH_2OEt \xrightarrow{Pd(II)} CH_3CH{=}CHOEt \xrightarrow{N_3CO_2Me} CH_3CH_2C(OEt){=}NCO_2Me \qquad (4)$$

The same imine can be formed almost quantitatively by non catalyzed reaction of the organic azide with the vinylic ether, and thus the palladium complex mainly catalyses the isomerization from the allylic ether to the corresponding vinylic ether. The rate of the catalyzed reaction was found to be first order each in the allylic ether and in the organic azide. The ease of formation of the imine from the allylic ether depends on the nature of the organic azide, decreasing in the order: $MeSO_2N_3 > MeCO_2N_3 > PhN_3$. The proposed mechanism involves the Pd(II)-catalyzed isomerization of allylic to vinylic ether as the rate determining step, but the real catalyst is thought to be $PdCl_2(PhCN)(N_3R)$, which however could not be detected. Allylic sulphides were also used as substrates.

Brønsted acids such as TfOH (Tf = triflate) promote the addition of electron-rich organic azides to activated olefins to give the corresponding aziridines [59]. However, it was concluded that the triazoline needs not to be an intermediate, contrary to



Scheme 22. Ref. [57].

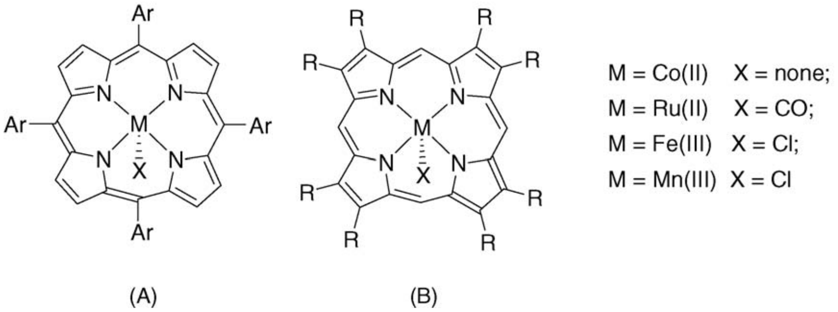


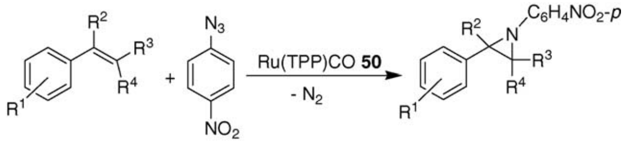
Fig. 12. Metal–porphyrin complexes: (A) aryl substituent in the *meso* position of the porphyrin ring and (B) alkyl substituent in the *beta* position of the porphyrin ring.

what invariably proposed in the preceding literature [1]. A possible transition state could be favored by an electron-withdrawing group on the olefin.

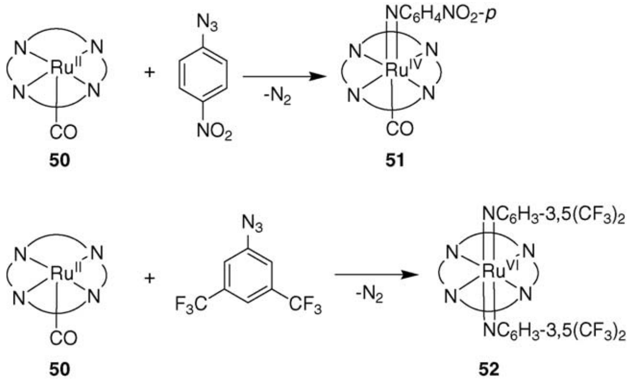
With transition metal complexes as catalysts, the situation is more complicated, but still the triazoline is not an intermediate leading to the aziridine. It has been reported that Cr(TPP) (TPP = dianion of 5,10,15,20-tetraphenylporphyrin) reacts with tosyl azide to give the corresponding nitrene complex, which is able to transfer the nitrene moiety to unsaturated substrates in stoichiometric reactions [60]. We therefore thought it possible to use transition metals porphyrin derivatives of as catalysts and organic azides as sources of the nitrene residue for the amination of olefins [61]. The results obtained have shown that this represents a simple procedure for the catalytic synthesis of allyl amines or aziridines in a selective way, with a high turnover number and under mild conditions. It is worth mentioning here that $TsN_3$ proved to be less efficient than TsN=IPh [62], the aminating agent usually employed with alkenes, when it was used with styrene as substrate and CuOTf as catalyst [63]. Note that compounds such as RN=IPh can be obtained only from the corresponding sulfonamides (that is $R = R'SO_2-$) and thus they belong to a limited family of reagents, while aromatic azides represent a wide class of easily synthesized compounds.

Metal–porphyrin complexes are fascinating molecules, which allow the exploration of the influence of the metal and of the substituents on the porphyrin ring on the outcome of the investigated reactions (Fig. 12).

The iron(III) and manganese(III) porphyrin complexes reported in Fig. 12 are the derivatives usually employed as catalysts in several reactions. We have used ruthenium(II) and, for the first time, cobalt(II) complexes as catalysts in the amination reactions of unsaturated and saturated (see Section 3.3) hydrocarbons. By using Ru(TPP)(CO) **50** as catalyst and $p$-$NO_2C_6H_4N_3$ as the organic azide, allylic amines or aziridines have been obtained, depending on the olefin employed as substrate (Schemes 23 and 24) [64].



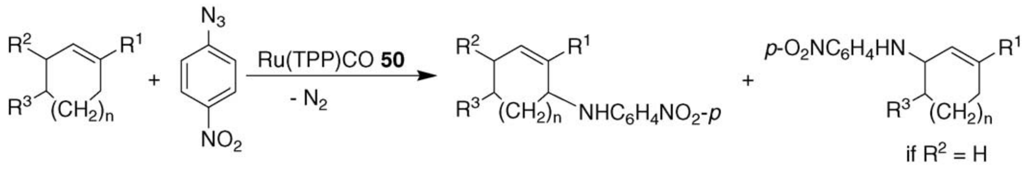
Scheme 24. Ref. [64].



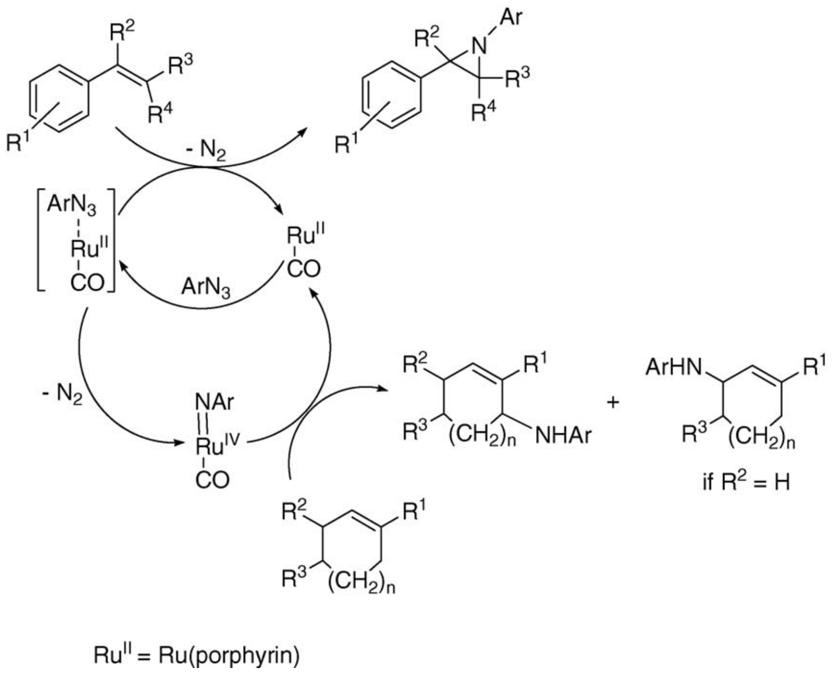
Scheme 25.

Cyclohexene (Scheme 23, $R^1 = R^2 = R^3 = H$; $n = 1$) reacts without a catalyst very slowly with $p$-$NO_2C_6H_4N_3$ to give the corresponding aziridine. One could speculate that the mechanism of reactions shown in Schemes 23 and 24 is similar, the only difference being the transition state, which in one case leads to the allyl amine and in the other to the aziridine. However, this is not the case. By reaction of Ru(TPP)(CO) **50** with $p$-$NO_2C_6H_4N_3$, we were able to isolate an imido complex **51** (Scheme 25).

By reaction with 3,5-$(CF_3)_2C_6H_3N_3$ the bis-imido complex **52** was obtained. The mono-imido complex **51** reacts with cyclohexene to give the allyl amine with a rate comparable to the catalytic one. On the other hand, α-methyl styrene reacts with **51** to give the aziridine at a much slower rate with respect to the



Scheme 23. Ref. [64].



Scheme 26.

one of the catalytic reaction. These data support the view that the imido complex **51** is an intermediate in the case of cyclohexene but not in the reaction with styrene. This is in accordance with the kinetic law observed in the case of cyclohexene (Eq. (5)):

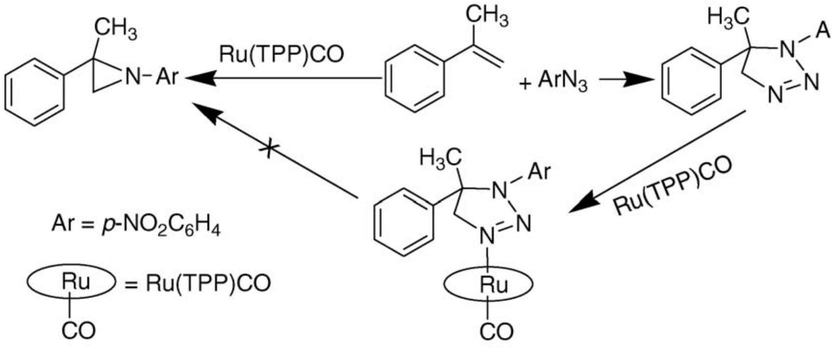
$$r = \frac{-\mathrm{d}[\mathrm{ArN_3}]}{\mathrm{d}t} = k[\mathrm{Ru(TPP)(CO)}][\mathrm{ArN_3}] \qquad (5)$$

That is, in this case, the rate law is independent on the olefin concentration and the rate determining step is the formation of the nitrene complex. On the other hand, the observed kinetic law in the case of α-methyl styrene (Scheme 24, $R^1 = R^3 = R^4 = H$; $R^2 = CH_3$) is more complex and depends on the olefin concentration (Eq. (6)):

$$r = \frac{-\mathrm{d}[\mathrm{ArN_3}]}{\mathrm{d}t} = k[\mathrm{Ru(TPP)(CO)}][\mathrm{ArN_3}][\alpha\text{-methyl styrene}] \qquad (6)$$

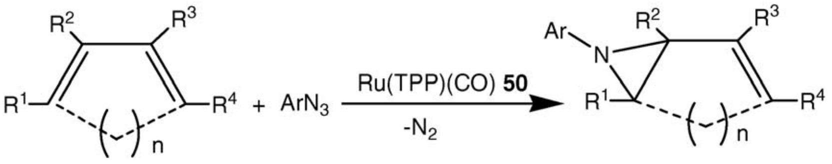
Moreover, the reaction deviated from that in Eq. (6) at high α-methyl styrene concentrations, where an inhibition effect by the olefin observed. A possible reaction mechanism is reported in Scheme 26.

It is proposed that the organic azide coordinates to the metal, and then the olefin attacks the coordinated organic azide in the aziridination step. This is in agreement with the fact that the organic azide acts as an electrophile in the catalytic cycle and, for example, $p$-$NO_2C_6H_4N_3$ is much more reactive than $p$-$OMeC_6H_4N_3$. When the reaction of the olefin with the coordinated organic azide is slow, the intermediate evolves to the imido complex, which then reacts with the olefins, as in the case of cyclohexene. During the reaction of α-methyl styrene with $p$-nitrophenyl azide the formation of 1,4-nitrophenyl-5-phenyl-1,2,3,-triazoline, outside the coordination sphere of the metal has been observed. This triazoline, which is very stable and it is not the intermediate leading to the aziridine, coordinates to the ruthenium center of the catalyst to give a complex **53** which decomposes only at temperatures above 250 °C (Scheme 27). The X-ray structure of this complex showed a coordination to ruthenium at the $N_\gamma$ nitrogen atom [65]. This explains why at



**53**

Scheme 27. Ref. [65].



Scheme 28. Ref. [67].

high concentration of the olefin the catalytic reaction is hampered, being the reactive center blocked by the triazoline which is now formed with a rate comparable to that of the catalytic formation of the aziridine.

By using Co(TPP) instead of Ru(TPP)(CO) as catalyst in the amination of α-methyl styrene, the situation is similar. The main difference is that the cobalt catalyst suffers the presence of the excess olefin only at much higher concentrations and up to now we were unable to isolate any imido complex from the reaction of $p$-$NO_2C_6H_4N_3$ with Co(TPP), nor the triazoline mentioned above coordinates to Co(TPP) in an irreversible way.

In the amination of cyclohexene with Co(TPP) as catalyst, the allyl amine is formed but the mechanism and the kinetic equation need to be investigated more deeply, since a significant amount of the azo derivative, $p$-$NO_2C_6H_4N{=}NC_6H_4NO_2$-$p$ is also formed.

Recently, we have also used the bis-oxo ruthenium derivative, $Ru(TPP)(O)_2$, as catalyst in the amination of olefins. This complex, for which the synthesis has been optimized and the reactivity towards CO and alkenes has been investigated [66], proved to be a better catalyst than Ru(TPP)(CO) **50**. We are also currently exploring the amination by aryl azides of conjugated dienes, catalyzed by Ru(TPP)(CO) (Scheme 28).

By the appropriate combination of the organic azide (electron poor) and the substituents on the diene (generally non cyclic) a complete selectivity in vinylaziridine was achieved, with a TOF of 80 $h^{-1}$ [67]. This is a very convenient method for the synthesis of organic compounds with two functional groups, which can be involved in a variety of reactions.

Terminal imido derivatives of manganese(V)-corrole derivatives have recently been isolated, but olefins are not reactive enough to accept a “NR” fragment from these complexes [68]. On the other hand stoichiometric reaction of a nitride manganese(V)–Schiff base complex in the presence of $Ts_2O$ gave monoaziridination of dienes [69].

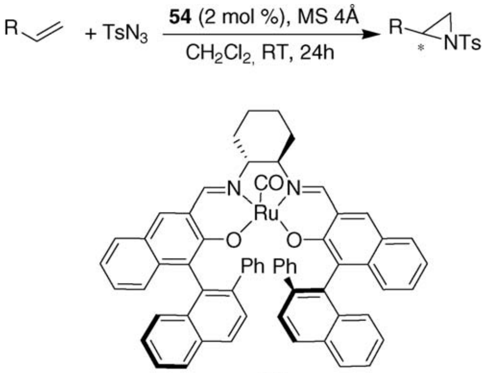
We have also attempted to employ chiral porphyrins [70] in the synthesis of optically active allyl amines and/or aziridines. Apart from tedious routes for their synthesis, the first results were either unsuccessful or moderately encouraging. For this reason, we used also other macrocycles such as Schiff bases like $acacenH_2$ ($acacenH_2$ = 2,11-dihydroxy-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene) [71], for which the synthesis of their chiral derivatives is more straightforward. However, a complex such as Co(II)(acacen) does not catalyze the reactions of organic azides with alkenes and it seems to react with the organic azide giving an inert system. However, it is a highly efficient catalyst for the allylic amination of non activated alkenes using $N$-($p$-toluenesulfonyl)iminophenyliodinane, TsN=IPh, as nitrene precursor [71].

The ($R$,$R$)-Ru(Schiff base)(CO) complex **54**, was found to catalyze the enantioselective aziridination of conjugated, terminal olefins and the allylic C–H amination of conjugated olefins bearing geminal and/or $trans$-substituents in the presence of $TsN_3$ [72] (Scheme 29).

The reactions examined proceed with high enantioselectivity. However, non conjugated terminal olefins such as 1-octene underwent neither aziridination nor allylic C–H amination. An intermediate ruthenium–nitrenoid species was suggested. More recently, the same research group reported on a new, robust fluorinated Ru(Schiff base)(CO) complex, which showed improved turnover numbers (up to 878) and enantioselectivities (up to 99%) in aziridination reactions of olefins, using $p$-toluenesulfonyl or $p$-nitrobenzenesulfonyl azides as the nitrene precursors [73].

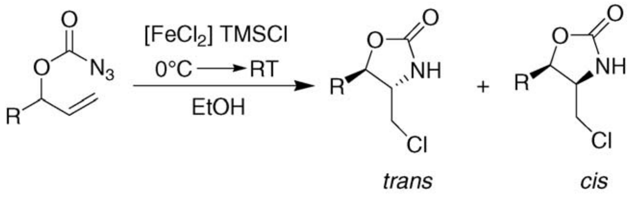
To the best of our knowledge, the only example of a metal catalyzed intramolecular amination of an olefin by an azido group, is the reaction of 2-alkenyloxycarbonyl azides, which in the presence of TMSCl and $FeCl_2$ as catalyst, afforded the corresponding 4-(chloromethyl)oxazolidinone (60–80% yield) presumably via a stepwise single electron transfer pathway. A prevalence of the $trans$-diasteroisomer was always observed [74] (Scheme 30).

The [3 + 2] cycloaddition reactions of metalla dipolarophiles with organic 1,3-dipoles, and of metalla 1,3-dipoles with organic dipolarophiles, have been discussed [75].

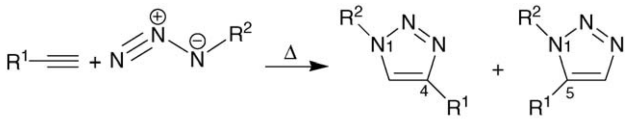


54

Scheme 29. Ref. [72].



Scheme 30. Ref. [74].



Scheme 31. Refs. [76,77].

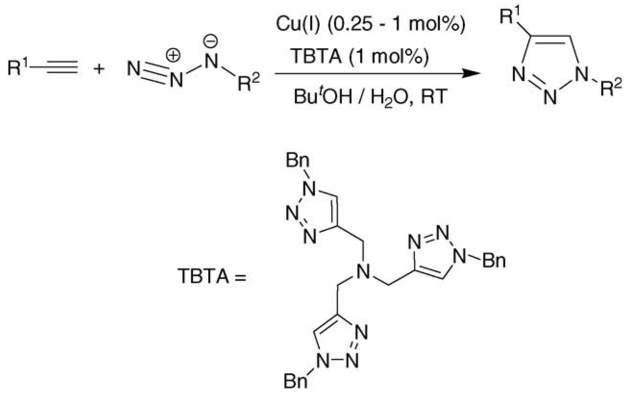
1,2,3-Triazole formation under mild conditions via 1,3-dipolar cycloaddition of acetylenes substituted with electron-withdrawing groups with organic azides, is an important route to a family of relevant compounds [76]. However, in the other cases the desired triazole forming cycloaddition may require elevated temperatures [77] and usually results in a mixture of the 1,4 and 1,5 regioisomers (Scheme 31).

In the presence of copper(I) as catalyst, the reaction sequence which regiospecifically unites organic azides and terminal acetylenes gives only 1,4-disubstituted-1,2,3,-triazoles [78]. The proposed reaction mechanism is reported in Scheme 32.

The intermediate formation of a copper(I)-acetylide is reasonable, especially because no reaction is observed with internal alkynes. However, the following stepwise ring formation sequence should lead to the six-membered copper-containing vinylidene intermediate A, and this proposal needs to be supported by some experimental evidence. More recently, this catalytic reaction has been applied to the synthesis of triazole dendrimers [79].

Polytriazoleamines were synthesized by the copper(I)-catalyzed ligation of organic azides and alkynes [80]. The $C_3$ symmetric derivative, TBTA, was shown to be a powerful stabilizing ligand for copper(I), protecting it from oxidation and disproportionation, while enhancing its catalytic activity (Scheme 33).

1,4-Disubstituted 1,2,3-triazoles are obtained in excellent yields by a convenient one-pot procedure from a variety of readily available aromatic and aliphatic halides without the isolation of potentially unstable organic azides intermediates [81a]. The synthesis of the organic azide in some cases and the formation of the 1,4-triazoles as well, are catalyzed by copper(I) derivatives, prepared in situ by reduction of copper(II) salts (Scheme 34).



Scheme 33. Ref. [80].

The mechanism of the ligand free Cu(I)-catalyzed organic azide–alkene cycloaddition reaction has been very recently studied [81b], and the application of the same reaction to the head-to-tail peptide cyclodimerization has also been reported [81c].

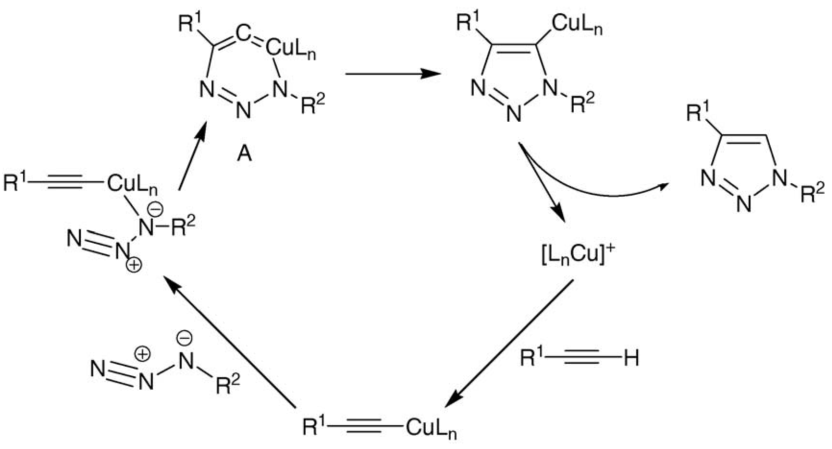
Analogous reactions performed under microwave irradiation were significantly accelerated [82]. The influence of several ligands of copper(I) on the rate of the reaction of organic azides with alkynes to give triazoles was investigated for a model reaction where the organic azide is a fluorophore. A dramatic disappearance of fluorescence was observed when the triazole is formed [83].

One-pot synthesis of *N*-sulfonylamidines has been realized by the copper(I)-catalyzed three-component coupling of sulfonyl azides, alkynes and amine [84] (Scheme 35).

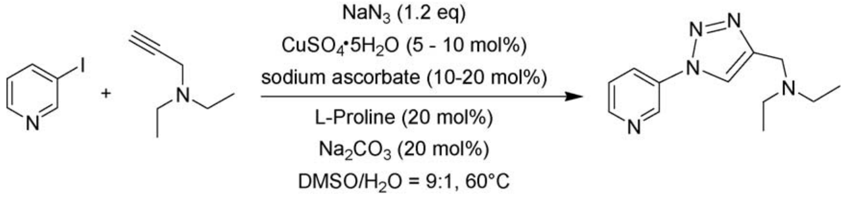
A plausible pathway proceeds through the intermediate formation of a copper–acetylide complex, followed by a nucleophilic attack on the $N_\alpha$ organic azide nitrogen to give a keteneimine species, which then rearranges in the presence of the amine to the final amidine (Scheme 36).

### 3.3. Reactions with benzylic derivatives

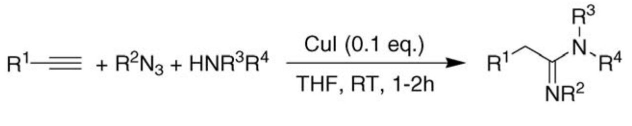
The reactions of hydrocarbons that contain a benzylic group with aromatic azides catalyzed by Co(II)(porphyrin) derivatives **55** leads to the formation of the corresponding amine [85] (Eq. (7)):



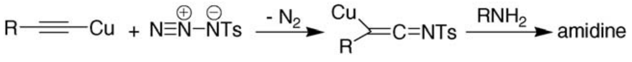
Scheme 32. Ref. [78].



Scheme 34. Ref. [81a].



Scheme 35. Ref. [84].



Scheme 36. Ref. [84].

$$\mathrm{ArR^1R^2CH + Ar'N_3 \xrightarrow[-N_2]{Co^{II}(porphyrin)\mathbf{55}} ArR^1R^2C{-}NHAr'} \tag{7}$$

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. (8)):

$$\mathrm{ArR^1HC{-}NHAr' + Ar'N_3 \xrightarrow[-N_2]{Co^{II}(porphyrin)\mathbf{55}} ArR^1C{=}NAr' + Ar'NH_2} \tag{8}$$

Main byproducts of the reaction are the organic azide-derived aniline and the diarylazo compound. The reaction is sensitive to the nature of the organic azide employed. With toluene as substrate, only in the case of *p*-cyanophenyl azide was the benzylamine observed among the products. With all catalysts, electron-withdrawing substituents in the *para* position of the aromatic azide generally increased the yields of the imine, except for the derivative having the *p*-$NO_2$ group, which consistently gave lower selectivities then expected based on the general trend. It should be noted that imines with the *p*-nitro substituent hydrolyze very easily even during the workup and gas-chromatographic analysis. Since most metal–porphyrin catalyzed amination reactions reported up to date afford the sulfonylamide as product, the use of $TsN_3$ and TsN=IPh as aminating agents was also been investigated. Tosyl azide gave a very slow reaction and tosyliminoiodinane was even less reactive. The reaction of *p*-$NO_2C_6H_4N_3$ with toluene catalyzed by Co–porphyrin complexes is practically suppressed when carried out in the presence of the spin-trap compound 2,2,6,6-tetramethyl-1-pyperidine-*N*-oxide (TEMPO). Since there is no reaction between the Co–porphyrin complex and TEMPO in the absence of the organic azide, this suggests that the unpaired spin density of the Co–porphyrin complex is partly localized on the organic azide nitrogen atoms in the intermediate complex.

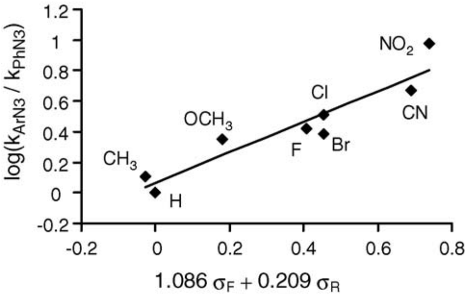
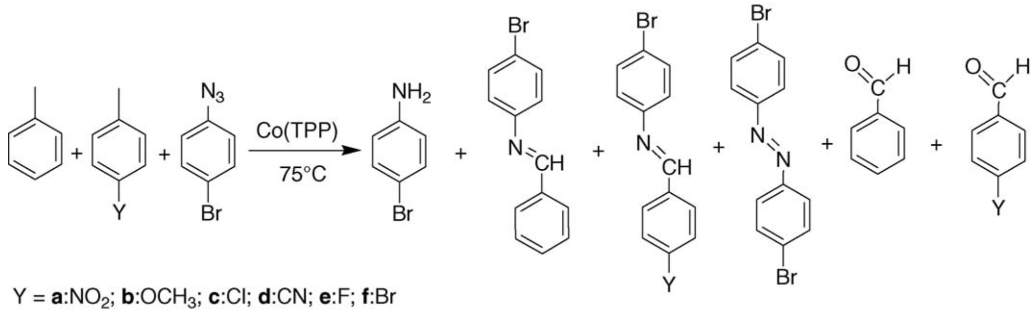


Fig. 13. Linear free energy correlation of $\log(k_{\mathrm{ArN_3}}/k_{\mathrm{PhN_3}})$ vs. Taft $\sigma_F$ and $\sigma_R$ parameters. The best fit for the equation $\log(k_{\mathrm{ArN_3}}/k_{\mathrm{PhN_3}} = \rho_F\sigma_F + \rho_R\sigma_R + c$ was found for the values $\rho_F = 1.086$ and $\rho_R = 0.209$ ($R^2 = 0.882$) [85b].

In a kinetic study, toluene was kept constant as a substrate, and the reaction rate for different organic azides was measured. A fair correlation was observed between the log of the ratio between the rate of the amination reaction with substituted organic azides and the rate of the corresponding reaction with phenyl azide and the Taft parameters (Fig. 13).

In a second series of experiments, different *para*-substituted toluenes were compared, keeping the organic azide constant. Competition experiments were run between the organic azide and an equimolar mixture of toluene and a substituted toluene (Scheme 37).

Being $k_r$ the ratio between the rate constant of the substituted toluenes and that of toluene, no correlation at all was found



Scheme 37. Ref. [85b].

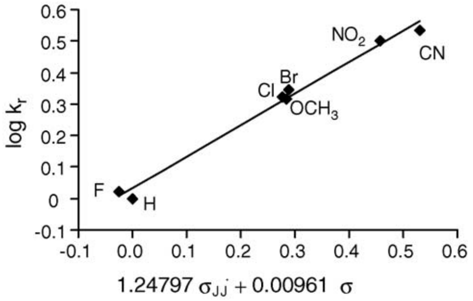


Fig. 14. Linear free energy correlation of $\log k_r$ (as defined in Eq. (9)) vs. ($\sigma_{jj}$, $\sigma$). The best fit for the equation $\log k_r = \rho_{jj}\sigma_{jj} + \rho\sigma + c$ was found for the values $\rho_{jj} = 1.24797$ and $\rho = 0.00961$ ($R^2 = 0.9887$) [85b].

between the $\log k_r$ values and the Hammet $\sigma$ or the related $\sigma^+$ constants. A good correlation could be obtained by the use of the $\sigma + \sigma_{jj}$ multivariate correlation, where $\sigma_{jj}$ describes the radical stabilization effect [86]. Eq. (9) with $\rho_{jj} = 1.25$, $\rho = 0.00961$ and $c = 0.0322$, describes the experimental values with $R^2 = 0.9887$ (Fig. 14):

$$\log k_r = \rho_{jj}\sigma_{jj} + \rho\sigma + c \tag{9}$$

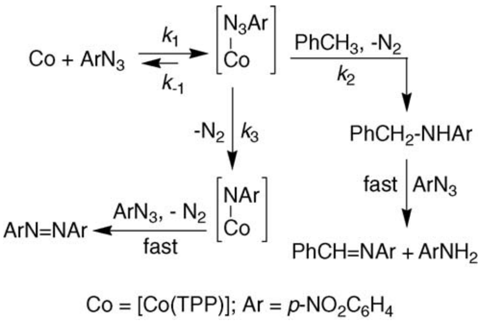
The overwhelming importance of the radical parameters is completely unprecedented. Indeed, the contribution of the polar parameter is so small (0.8% of that of the radical) that neglecting it completely gives an indistinguishably good fit ($R^2 = 0.9885$). The isotopic effect on the benzylation reaction was measured by running a reaction analogous to the preceding ones, but with deuterated toluene in place of the substituted toluene. The primary isotopic effect determined, $k_H/k_D = 14$, is again a value outside the normal range (usually 1–7).

All the collected kinetic data, could be explained by the reaction pathway shown in Scheme 38.

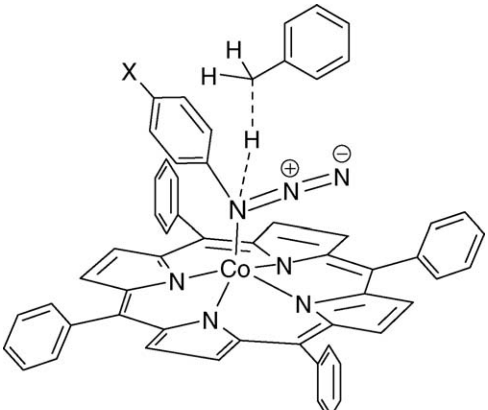
Application of the steady state approximation to the intermediate aryl azide–porphyrin complex leads to Eq. (10), which nicely fits the reaction rates observed at different toluene concentrations:

$$K_{\text{app}} = \frac{2k_1(k_2[\text{toluene}] + k_3)}{(k_2[\text{toluene}] + k_3 + k_{-1})} \tag{10}$$

The proposal of an aryl azide 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/Schiff base-catalyzed sulfimidation of sulfides [87] and in the Mn/porphyrin-catalyzed aziridination of olefins [88]. 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 data reported on Fig. 13, we can conclude that the nitrogen atom of the organic azide acts as an electrophile in the transition state, which is not surprising. The anomalous importance of radical stabilization effects in the toluene series is paralleled by the very high isotopic effect. In general, $k_H/k_D > 12$ at 25 °C are considered to be a reliable evidence for tunneling [89,90] and can be observed when the reaction involves the transfer of an hydrogen atom that should pass through a very high energy barrier. Thus, an $^1$H atom can pass the barrier by tunnel effect much more easily than a deuterium atom will, giving rise to an high observed isotopic effect. On these bases, the transition state **56** reported in Fig. 15 was proposed.

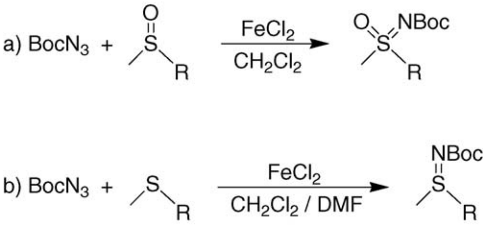


Scheme 38. Ref. [85].



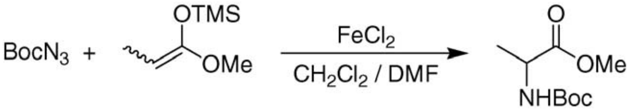
**56**

Fig. 15. Proposed transition state for the amination reaction [85b].

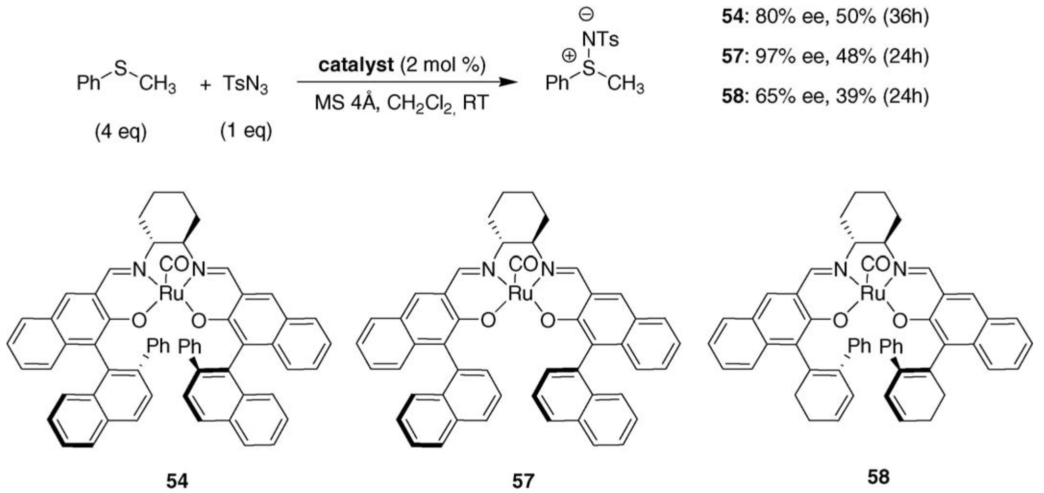


Scheme 39. Ref. [91].

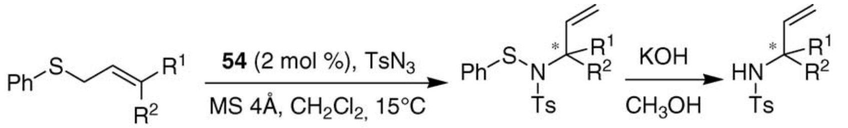
The pocket conformation of the aryl azide makes steric hindrance very severe for the incoming toluene molecule and we can say that it prevents the reacting molecules from approaching each other up to the correct distance for the hydrogen atom transfer to occur in a classical way. Thus, the hydrogen atom has to do a “long jump” that is characterized by a high energy barrier, since during the travel it loses most of the stabilization



Scheme 40. Ref. [93].



Scheme 41. Ref. [94].



Scheme 42. Ref. [95].

due to the breaking bond, without gaining significantly through the new bond formation.

The amination of the C–H bond of toluene has also been attempted by using Co(II)(acacen) as catalyst [72]. However, only by using TsN=IPh as aminating agent the formation of the corresponding sulfonamide was observed.

### 3.4. Reactions with sulfur-containing compounds

The nitrene transfer from *t*-butyloxycarbonyl azide ($BocN_3$) to several nucleophiles is promoted by iron(II) chloride and yields the corresponding N-Boc protected sulfoximides or sulfimides [91] (Scheme 39).

The stereospecificity of the reaction was demonstrated by using enantiomerically enriched substrates, obtaining sulfoxamides with retention of configuration [92]. An intermediate $Fe^{IV}$(nitrene) complex was postulated as the reactive nitrene transfer reagent which is formed from $FeCl_2$ and $BocN_3$. The reaction was extended to allyl aryl sulfides [93].

Preliminary experiments have been performed with carbon nucleophile, and with an electron-rich ketene acetal an α-amino alkanoate was obtained, although in low yields (Scheme 40).

Ru(Schiff base)(CO) complexes **54**, **57**, **58** were found to catalyze the imidation of alkyl aryl sulfides in the presence of arylsulfonyl azide with high enantioselectivity as well as good chemical yields [94] (Scheme 41).

Asymmetric C–N bond formation was achieved in a highly enantioselective manner by using Ru(Schiff base)(CO) **54** catalyzed sulfimidation and the subsequent [2,3]sigmatropic rearrangement [95]. Treatment of allyl aryl sulfides with $TsN_3$ in the presence of the ruthenium catalyst, followed by hydrolysis of the resulting *N*-allyl-*N*-arylthio toluene sulfonamides provided *N*-allyl toluenesulfonamides in high enantiomeric excesses (Scheme 42).

Enantioselective imidation of alkyl aryl sulfides with *N*-alkoxycarbonyl azides as nitrene precursors was effected with the same catalyst [96]. The steric and electronic nature of the *N*-alkoxycarbonyl group was found to strongly affect the enantioselectivity and the reaction rate, and high enantioselectivities (up to 99% ee) and good chemical yields were achieved by using 2,2,2-trichloro-1,1-dimethyl-dimethylethoxycarbonyl azide as the nitrene precursor at room temperature.

## 4. Conclusions

The high reactivity of organic azides means that few complexes with an intact azide as ligand have been isolated and characterized by X-ray methods. However, coordination to the metal through the $N_\alpha$ atom of the azido group, which is the most basic, is not a general feature in these complexes. In many cases the coordination at the terminal $N_\gamma$ atom is preferred. This has been attributed, in the case of a copper(I) derivative with respect to a silver(I) complex, to a better coordination, favoring a π-back bonding from the metal to the organic azide (see Section 2.1), although it not clear which orbitals can be used by the azido group. Moreover, this consideration is not valid in the case of tantalum(V), vanadium(V), zirconium(IV) and tungsten(VI) complexes, being the metals in a high oxidation state. This way of reasoning is a formalism, since in the last cases we consider the organic azide as a −2 diazenimido ligand, while for the copper(I) derivative a neutral azido donor group is considered. This situation is reminiscent of what has been thoroughly discussed in the past for aryldiazonium complexes [97]. As far as the reactions of organic azides with coordinated ligands is concerned, we can draw some general conclusions. With anionic ligands such as the hydrides, the azido group acts as an electrophile, attacking the ligand via the $N_\gamma$ atom. Electrophilic reactions have also been observed in the interaction with carbon monoxide, catalyzed by $RhCl(CO)(PR_3)_2$ and related complexes under mild conditions and with high selectivity. In fact, these reactions are favored by electron-withdrawing substituents on the aromatic azide and basic ligands on the metal complex. However, in these cases the reaction probably proceeds trough the attack of the organic azide to the metal, followed by insertion of carbon monoxide in the $M–N_\alpha$ bond (see, for example, Fig. 4), with extrusion of dinitrogen. It is useful to remind that the reaction of aromatic azides with carbon monoxide in the absence of the metal, is favored by +M substituents in the *para* position of the organic azide, which should stabilize the presumed "nitrene" intermediate. Moreover, the reaction requires harsh conditions and it is not selective. In other cases, the organic azide acts as a nucleophile with attack to the carbon atom of coordinated carbon monoxide by the $N_\alpha$ atom. It should be noted that in these cases the intermediate is stabilized by coordination of $N_\gamma$ to another metal center (see Schemes 4–6). With coordinated phosphines, the attack at $N_\gamma$ by the phosphorus atom is observed, and thus the organic azide acts again as an electrophile. Electrophilic attack of coordinated ligands at $N_\gamma$ is also observed with the single metal–carbon bond. With metal–nitrene complexes, the expected 1,3-dipolar cycloaddition is the dominant reaction, with $N_\alpha$ attacking the metal and $N_\gamma$ the imido nitrogen. Too few examples are known of the reactions with metal–carbene complexes to attempt any general conclusion. However, the known examples involve the insertion of the nitrene residue into the metal–carbene bond.

One of the most important features of the catalytic reactions of organic azides with alkenes is that the primary products are the corresponding aziridines or allylic amines and not the triazolines, as observed in the organic reactions. Moreover, with electron poor olefins the reactivity of the organic azide increases in the order: $p\text{-MeOC}_6H_4N_3 > PhN_3 > p\text{-NO}_2C_6H_4N_3$. On the other hand, the opposite reactivity order is observed for all transition metal-catalyzed reactions.

We can conclude that the action of transition metal catalysts in the reactions of organic azides is that of accelerating and in general orienting these reactions in a way different from those observed in the pure organic reactions, and this represents a useful assistance for the synthetic chemist. Moreover, of particular relevance are the reactions where chiral catalysts are used, which allow the formation of optically active products with high yields and high enantiomeric excesses, one among the most significant subjects in modern organic synthesis.

## Acknowledgement

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