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Carbon monoxide as a selective reducing agent in organic chemistry

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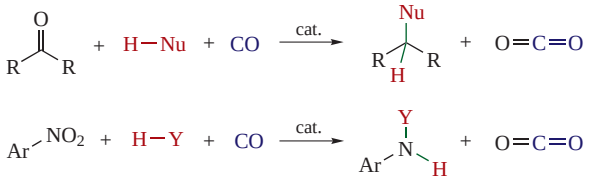
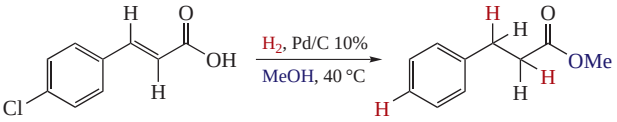
Carbon monoxide as an example of reducing agent, in contrast to classical reducing agents (hydrogen and metal hydrides), can provide very high atom precision for reductive addition of substrates with various functional groups. This enables synthesis of new compounds with unique structures and properties.



Introduction

The most rational concept for chemical synthesis suggests that in an ideal chemical process all atoms present in the starting materials are converted into the atoms of the target products. In order to achieve this, it is necessary to develop highly effective catalytic procedures, which transform simple building blocks into complex organic molecules. In case of industrial applications, it is also highly desirable to use accessible and inexpensive components. Reductive transformations are irreplaceable in various synthetic processes, and usually a source of hydrogen, which means a hydride agent or hydrogen gas itself, is required to conduct them. Reductions with hydrogen gas clearly fit atom-economical principle. However, when hydrogen-based reductions are considered, only energy waste for the reduction itself is analyzed, but not the one for production of the reducing agent. In case of H_2, steam methane reforming is used to produce it from natural gas, which requires two steps, high temperatures (up to 800 °C) and separation of a gas mixture. For production of hydride reductants, multiple stages are required, which is not economically advantageous. The other problem of using H_2 gas is low selectivity. In case of reduction by H_2 gas, important functional groups can be hydrogenated (Scheme 1). Instead of simple hydrogenation of double bond, reduction of even carbon–chlorine bond can occur under mild conditions.[1]



Scheme 1 An example of low atom precision of molecular hydrogen.

In this context we became interested in the application of hydrogen-free systems for the reductive addition reactions. For molecules with an element–oxygen double bond we envisioned

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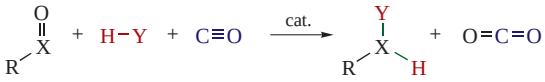
Scheme 2 Reductive addition without an external hydrogen source.

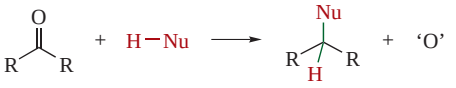
that a reaction with a hydrogen-containing reagent can be done in one step without the use of an external hydrogen source (Scheme 2). Fundamentally, such process needs nothing but an appropriate catalyst and a scavenger of the oxygen atom. The advantages of this approach include not only economy of atoms and steps; more importantly, very high atom precision[2] can be achieved, since some functional groups sensitive to dihydrogen or other hydride sources can survive under hydrogen-free conditions.

In contrast to classical reducing agents, carbon monoxide can provide selective reductive addition for substrates with various functional groups The simplest and the most atom-economical way is to use carbon monoxide as a reducing agent and the scavenger of the oxygen atom. In this case the only byproduct is carbon dioxide (Scheme 3). The gases can be released; therefore, almost no purification might be needed.

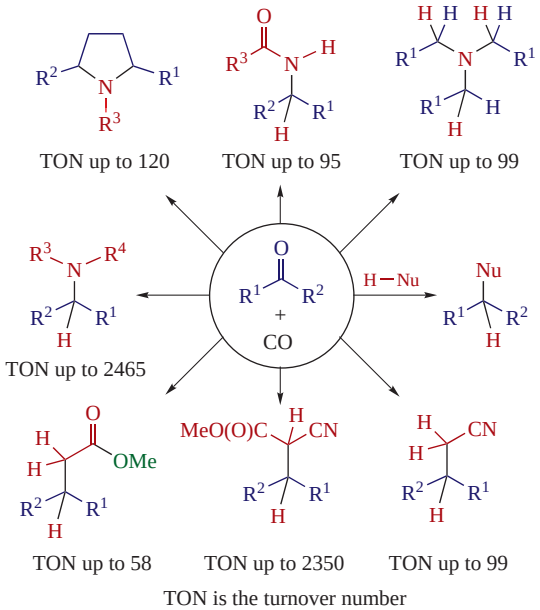


Scheme 3 Carbon monoxide as scavenger of the oxygen atom.

The approach can be divided into two aspects. The first one involves reactions of carbonyl compounds with hydrogen-containing nucleophiles (Schemes 4, 5). The second one implies reactions of aromatic nitro and nitroso compounds with hydrogen-containing electrophiles (Schemes 6, 7). Here carbon monoxide is used as a reductant in the synthesis of aromatic amines, N-heterocycles, carbamates, ureas, *etc*. from nitroaromatics.[3,4] Several cases in which CO/H_2O system is used as a reducing agent have been reported.[5] In this review, we do not consider these processes, because overall, they include an external hydrogen source.

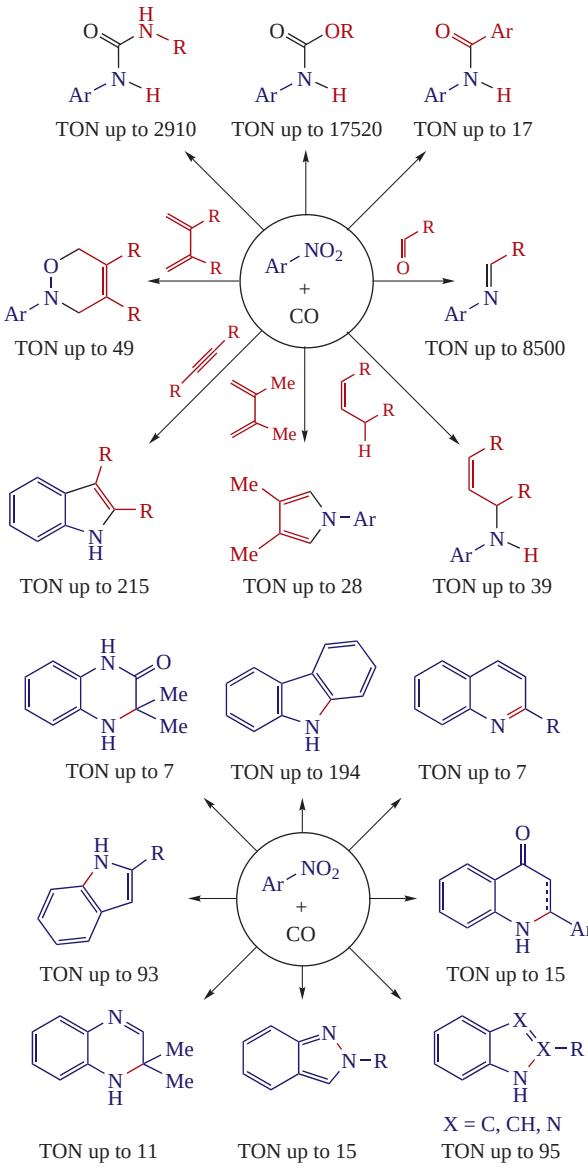


Scheme 4 Approach 1. Reductive addition to the carbonyl group without an external hydrogen source.



Scheme 5 Scope of reductive addition to the carbonyl group without an external hydrogen source.

Scheme 6 Approach 2. Reductive addition to the nitro group without an external hydrogen source.



Scheme 7 Scope of reductive addition to the nitro group without an external hydrogen source.

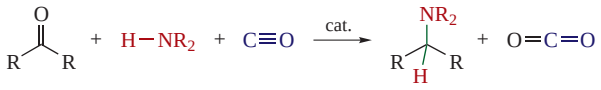
Approach 1

1.1. Reductive amination. Traditionally, the transformation proceeds in two steps: generation of a Schiff base and water and hydrogenation of the Schiff base. Direct reductive amination is also known; however, its biggest problem is that most of the reducing agents can reduce the starting carbonyl compound as well.

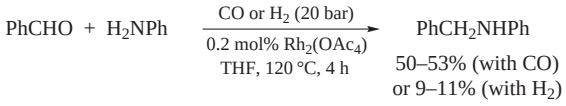
In the initial work, we showed that rhodium acetate can catalyze direct reductive amination without an external hydrogen source[6] (Scheme 8, Table 1). Various combinations of carbonyl compounds and amines afford the products in 70–98% yields. The reaction tolerates different functional groups, including aromatic nitro group. Interestingly, when dihydrogen gas was used instead of carbon monoxide, the yield of the desired product was five times less (Scheme 9). Moreover, in case of dihydrogen some byproducts were detected, *e.g.* reduction of the starting aldehyde to the alcohol. Mechanistic studies showed that at least the main process is not related to dihydrogen production. An important

Table 1 Different type of catalysts for the reductive amination without an external hydrogen source.

Entry	Catalytic system	CO pressure/ bar	Solvent	T/°C	t/h	Yield (%)	TON up to	Reference
1	0.2 mol% $Rh_2(OAc)_4$	20	THF	120–140	4–15	70–98	490	6
2	0.008–2 mol% $RuCl_3$	50	MeCN	140	22	70–99	2465	7
3	0.08–1 mol% Rh/C_{matrix}	50	THF	160	20	64–99	2449 (for 3 cycles)	8
4	0.05–2 mol% $(C_4Et_4)Rh(xylene)PF_6$	3	EtOH	90	12–100	67–99	1340	9
5	1 mol% $[CpIrI_2]_2$	30	THF	150	20	62–96	96	10
6	1 mol% $IndRhI_2$	30	H_2O	120	4	83–98	98	11



Scheme 8 Different type of catalysts for the reductive amination without an external hydrogen source (Table 1).



Scheme 9 Reductive amination with carbon monoxide *vs*. molecular hydrogen.

advantage of this approach is that a simple rhodium salt without any ligand is sufficient as a catalyst. The disadvantage of this protocol was the necessity to use expensive rhodium. Thus, for broader synthetic applications the activity of the catalyst has to be increased or alternatively other less expensive metals should be used instead of rhodium. Additionally, the reaction temperature and pressure left room for improvement.

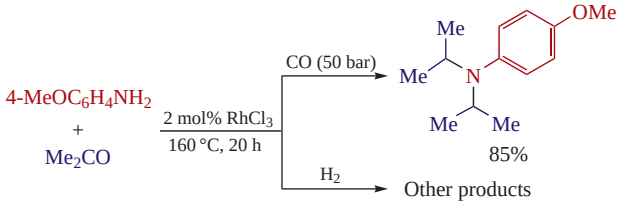
Since industry prefers heterogeneous catalysts, we adapted the new reaction for the use of heterogeneous rhodium catalysts.[8] The advantage of this modification is reusability of the catalyst with total TON up to 2449. The disadvantages include higher temperature (up to 160 °C) and high pressure (50 bar).

Other metals can also be implemented in this process. Whereas no examples of effective use of palladium or platinum in this reaction have been reported,[6] iridium catalysts can be successfully employed.[10,12] Halide ligands on iridium increase the catalytic activity in the range Cl < Br < I. Even simple addition of sodium iodide to iridium trichloride increases the activity of the catalytic system 1.5 times. Iridium catalysis enables full compatibility with a range of functional groups prone to reduction (*e.g.* *N*-benzyl, dioxolane, halogen, cyclopropanes).

The price of ruthenium is one order of magnitude less than the price of rhodium, iridium, palladium or platinum. Therefore, we were delighted to find that simple ruthenium trichloride without any ligand can successfully catalyze the reductive amination.[7] The method was applied to a one-step synthesis of anti-anxiety agent Ladasten comprising a bulky ketone and aromatic amine containing labile bromine atom.

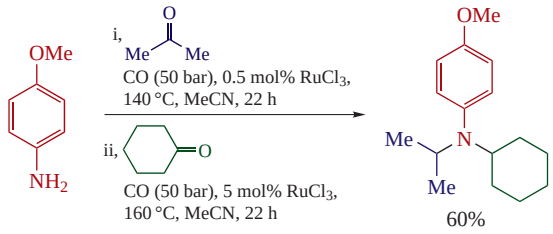
The use of bulky ketones in reductive amination is a particularly challenging problem, especially for mild and selective reducing agents such as triacetoxyborohydride.[13] The situation changed with the report of a general approach to the synthesis of these compounds with the use of carbon monoxide as a reducing agent.[14] The developed methodology allows one to conduct the reaction even with poorly nucleophilic diphenylamine. The general trend is that rhodium catalysis works better for more nucleophilic amines, whereas ruthenium catalysis demonstrates better performance with less nucleophilic amines. The phenolic moiety can be tolerated without protection, which might be the problem in case of classical hydride reagents.

The use of dihydrogen gas under the same conditions did not afford the desired product. Instead, hydrogenation of aromatic ring was observed (Scheme 10). This shows that reduction of a very stable aromatic ring is still easier than reductive formation



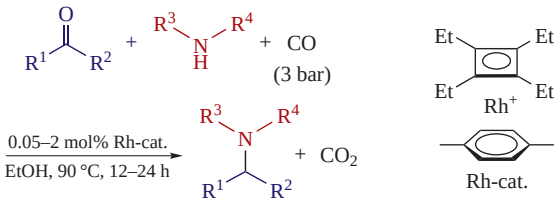
Scheme 10 Reductive amination with carbon monoxide *vs*. molecular hydrogen.

of sterically hindered amines for a classical system with dihydrogen gas. Moreover, a one-pot approach to the synthesis of unsymmetrical sterically hindered tertiary amines from a primary amine and two different ketones was demonstrated (Scheme 11).



Scheme 11 One-pot approach to the synthesis of unsymmetrical sterically hindered amines.

The use of cyclobutadiene rhodium complexes enabled development of an unusually mild protocol for direct reductive amination, which is compatible with a wide range of functional and protective groups, including those conventionally unstable under reductive conditions (Scheme 12). The required pressure and temperature vary from 1 to 3 bar and from 75 to 100 °C.[9,15] Table 2



Scheme 12 Reductive amination in the presence of cyclobutadiene rhodium complex.

Table 2 A generalized comparison of functional/protective group stability under reductive conditions.

Group	Reductive system				
	H_2/Ni	H_2/Rh	$LiAlH_4$	$NaBH_4$	Rh-cat./CO
R_2N–Cbz	–	–	–	+	+
R_2N–C(O)CF_3	–	+	–	–	+
R_2N–Bn	–	–	+	+	+
RO–Bn	–	+	+	+	+
Ar–NO_2	–	–	–	±[a]	+
Ar–CN	–	–	–	±[a]	+
Ar–Br	–	+	±[a]	+	+

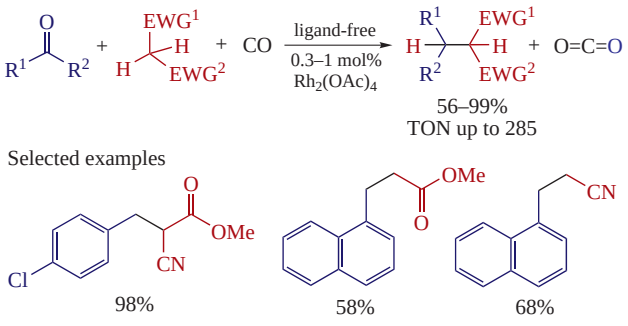
[a] ± means that both results can be found in literature.

compares compatibility of various synthetically important functional groups with a number of common reducing conditions, including the catalytic methodology described herein. Whereas the lability of functional groups is certainly substrate- and condition-dependent, the general trends clearly demonstrate the unique synthetic utility of the CO-assisted catalytic system. Moreover, the new approach was compared with a complex hydride of high functional group tolerance which is conventionally used for reductive amination, namely, sodium cyanoborohydride ($NaBH_3CN$). For an arbitrarily chosen subset of substrates considerably higher yields of the desired products using CO system were observed (88–98% yields) *vs.* sodium cyanoborohydride (33–68%).

The same chemistry was used for the synthesis of chiral ligands, namely salan ligands.[16] In contrast to the traditional two-step protocol, the reaction proceeds in one step. The prepared diamines were used as organocatalysts for a two-step synthesis of α-hydroxy γ-keto esters from arenes, chlorooxoacetates and ketones, as well as chiral ligands for Meervein–Ponndorf–Verley reduction and Henry reaction. An ammonium salt can be used as a source of amine without isolation and purification of the amine.

To sum up, reductive amination without an external hydrogen source can be catalyzed by rhodium, ruthenium and iridium complexes. Usually, the activity of catalysts increases in the range Ir[10,12] < Ru[7] ≤ Rh.[6,9,11,17] For amines of low nucleophilicity, ruthenium catalysts give better yields in comparison to rhodium ones. The reactions proceed well in the range 75–180 °C, 1–100 bar. The highest TON up to date does not exceed 2500.

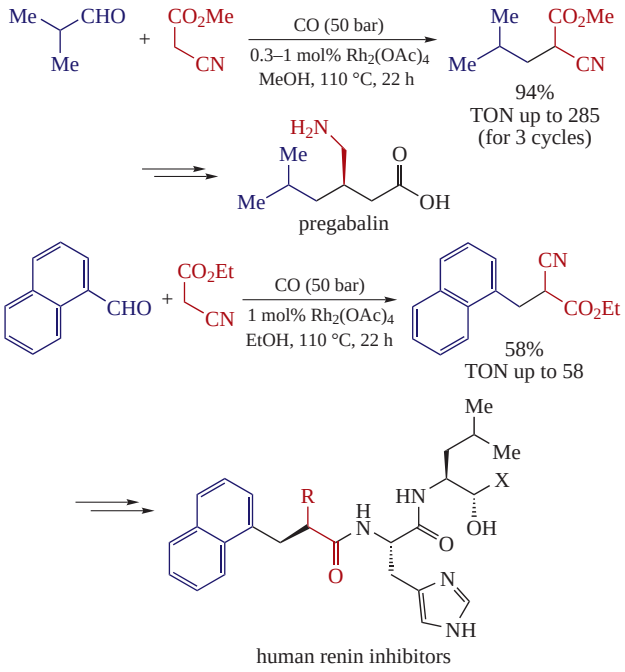
1.2. Reductive alkylation of C–H bond with carbonyl compounds. In 2014, the potential of Approach 1 in reductive alkylation of C–H bond with carbonyl compounds was described.[18] The developed methodology shows a possibility of reductive alkylation of various aldehydes/ketones with active methylene compounds (Scheme 13). The use of malonic acid or cyanoacetate as active methylene counterpart enables efficient formal deoxygenative addition of methyl acetate or acetonitrile to aldehydes. Synthetic utility of the developed methodology was exemplified by the synthesis of precursors of biomedically important compounds, such as peptidic human renin inhibitors and pregabalin (Scheme 14).



Scheme 13 $Rh_2(OAc)_4$ catalyzed reductive alkylation of C–H bond with carbonyl compounds.

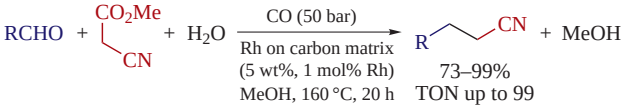
1.3. Tandem transformations. Based on this finding, the authors further expanded the strategy to formal reductive addition of acetonitrile to aldehydes with formation of nitriles.[8] The tandem process includes reductive alkylation, hydrolysis of ester moiety and decarboxylation. Despite harsh conditions and three consecutive steps the yields are surprisingly very high and a lot of functional groups remain intact (Scheme 15).

Other tandem transformations using reductive addition without an external hydrogen source were also discovered. The reaction of cyclopropyl ketones with amines affords either pyrrolidines or cyclopropyl amines.[19] The direction of the process can be altered

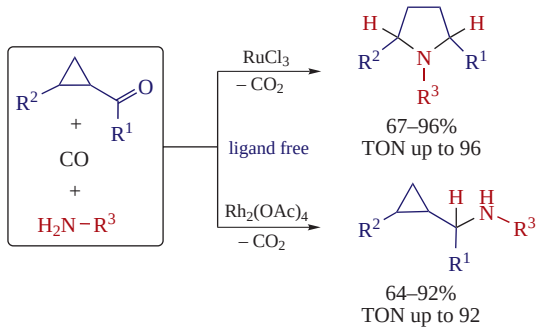


Scheme 14 Synthesis of precursors of pregabalin and human renin inhibitors *via* reductive alkylation.

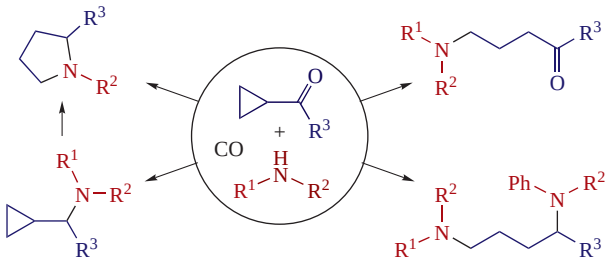
by simple changing catalyst from ruthenium trichloride to rhodium acetate (Scheme 16). Further investigation showed that reaction of cyclopropyl ketones with amines can also lead to amino ketones and diamines[20] (Scheme 17).



Scheme 15 Formal reductive addition of acetonitrile to aldehydes.

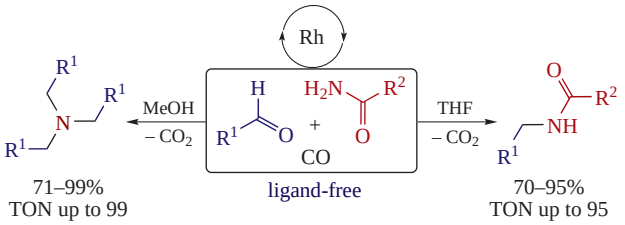


Scheme 16 Pyrrolidines *vs.* cyclopropyl amines formation in reaction of amine with cyclopropyl ketones.



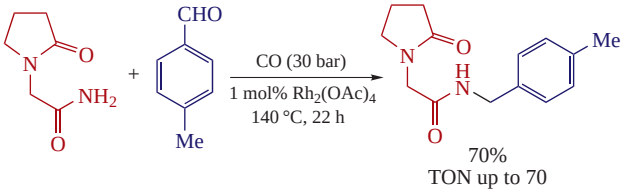
Scheme 17 Other transformations of cyclopropyl ketones with amines.

1.4. Reductive amidation. Primary amides have low nucleophilicity so their successful application in Approach 1 seems unlikely. Despite it, two reports revealed such a possibility.[21,22] Rhodium acetate itself can catalyze the process; surprisingly,



Scheme 18 Amide *vs*. tertiary amine formation in reaction of amides with aldehydes.

the direction of the reaction can be changed to the formation of symmetric tertiary amines simply by changing the solvent from tetrahydrofuran to methanol (Scheme 18). By this procedure a modification of piracetam was obtained (Scheme 19).

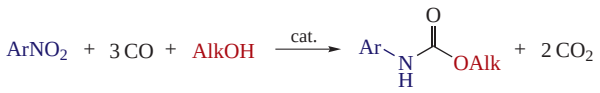


Scheme 19 Synthesis of a modification of piracetam.

Further detailed studies showed the possibility to use various ruthenium-based catalysts in reductive amidation without an external hydrogen source.[22] Ruthenium-catalyzed reaction works generally well (TON up to 93, yields 25–93%), although aldehydes with electron-withdrawing groups furnish the products in low yields. Unfortunately, no promising results with heterogeneous catalysts were found.

Approach 2

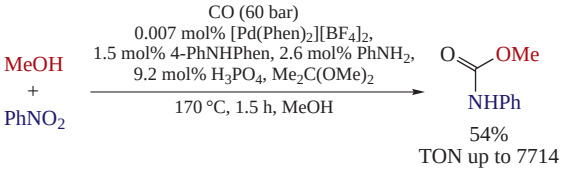
2.1. Synthesis of carbamates. The classical route to carbamate synthesis requires the use of dangerous phosgene. One of the alternatives is direct carbonylation of nitro compounds with carbon monoxide in the presence of alcohols (Scheme 20).



Scheme 20 Reductive carbonylation of nitrobenzenes to carbamates.

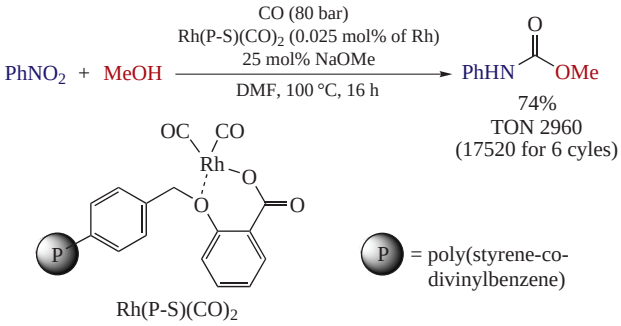
Different ruthenium,[23–32] rhodium,[27,28,33–38] palladium[39–72] and platinum[73–75] catalytic systems were developed for reductive carbonylation of nitrobenzene to carbamates. Catalytic systems which are not based on the use of noble metals were also applied, although their activity was considerably lower.[76–78] At the moment palladium-based systems represent the most explored class of catalysts in reductive carbonylation of nitroaromatics to carbamates. In early reports it was shown that nitrogen bidentate ligands like 1,10-phenanthroline are essential to achieve high conversion and selectivity. So far, a catalytic system with 4-anilinophenanthroline is the most active among palladium systems with TON over 7700 (Scheme 21).[57]

The most active catalytic system for reductive carbonylation reported by Mukherjee[38] consists of rhodium(I) complex



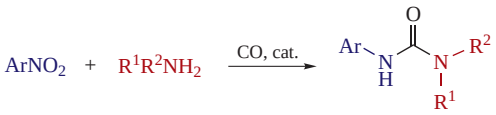
Scheme 21 Palladium-catalyzed synthesis of carbamates.

[Rh(P-S)(CO)$_2$] (P-S is polymer anchored salicylic acid) and NaOMe as a co-catalyst (Scheme 22).[38] This system can be successfully reused up to 6 times without significant loss of the product yield. For more detailed review of catalytic systems for carbamate synthesis, see Online Supplementary Materials.



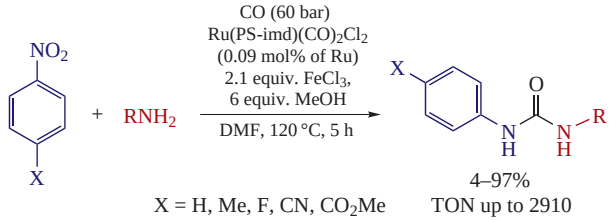
Scheme 22 Rhodium-catalyzed synthesis of carbamates.

2.2. Synthesis of ureas. Synthesis of ureas classically involves the use of phosgene which is dangerous. As in case of carbamate synthesis, ureas can be synthesized from nitro compounds in the presence of amines (Scheme 23).



Scheme 23 Synthesis of ureas.

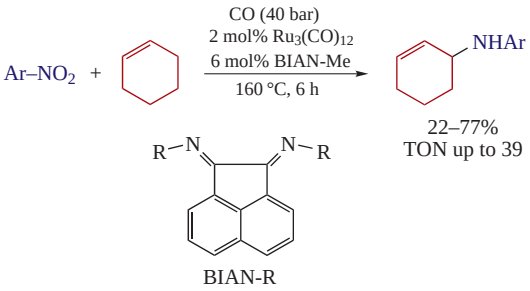
Palladium,[79–86] platinum,[87] ruthenium,[88–90] rhodium[91] and seleneium[92–97] catalytic systems were developed for this transformation. The most active catalytic system suggested by Islam *et al.* involves polystyrene-supported complex, [Ru(PS-imd)(CO)$_2$Cl$_2$] (PS-imd is polystyrene anchored imidazole) (Scheme 24).[90] *para*-Substituted nitrobenzenes and aromatic as well as aliphatic amines were successfully transformed to the corresponding ureas. For more detailed review of catalytic systems for urea synthesis, see Online Supplementary Materials.



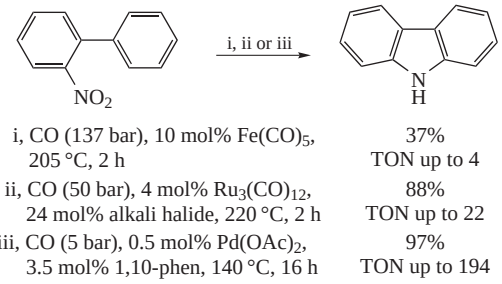
Scheme 24 Ruthenium-catalyzed synthesis of ureas.

2.3. Allylic Addition. While studying synthesis of diphenylurea from nitrobenzene in the presence of alkene, formation of allylamine was observed.[88,89] It was already mentioned above that nitrobenzene can be added to allylic position of an alkene albeit in very low yields (<10%). Later, the use of $Ru_3(CO)_{12}$ with BIAN-Me [BIAN is bis(imino)acenaphthenequinone] as an additive was suggested (Scheme 25). Different substituted nitrobenzenes were tested, and the best results among them were achieved for nitrobenzenes with electron-acceptor groups.[98,99] In case of cyclooctene, cyclopentene and α-methylstyrene, yields were almost twice lower. BIAN-Ph proved to be an even more active additive for this transformation.[100] Among other additives some chiral bis-oxazolines were tested, although the activities were lower and no enantioselectivity was observed.

In 1998, Nicholas *et al*. reported another catalytic system for allylic addition with [CpFe(CO)$_2$]$_2$ as catalyst (Scheme 26).[101]

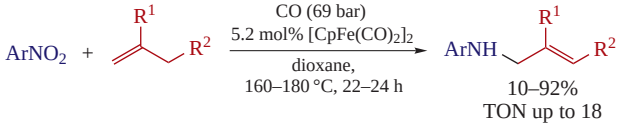


Scheme 25 Ru-catalyzed allylic amination.



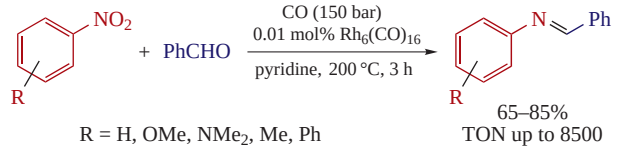
Scheme 28 Synthesis of carbazole.

Among various alkenes the most active one was α-methylstyrene which gave 92% yield in the reaction with nitrobenzene. For other alkenes the yields were generally at least twice as low. Nitrobenzenes with electron-acceptor groups were more active than those with electron-donor ones, although unsubstituted nitrobenzene was the most active. Later, $[Cp^*Fe(CO)_2]$ was also shown to be suitable for this transformation. Although activity of this complex was almost the same, its use made it possible to identify new carbonyl species which may be intermediates in this reaction.[102] The same transformation can also be promoted photochemically if $[Cp^*Fe(CO)_2]$ is used.[103]



Scheme 26 Fe-catalyzed allylic amination.

2.4. Synthesis of Schiff bases. In 1972, Iqbal reported direct synthesis of Schiff bases from aromatic nitro derivatives, aldehydes and CO (Scheme 27).[104] Different substituted nitrobenzenes gave corresponding Schiff bases in moderate to high yields, although the conditions were rather harsh. Formation of a Schiff base was also reported by Watanabe and coworkers on application of 5 mol% $Pd(PPh_3)_2Cl_2$, 0.5 equiv. $SnCl_2$ (71%, TON 14).[105]



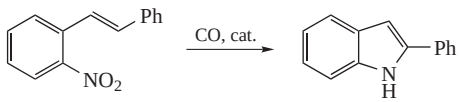
Scheme 27 Rh-catalyzed Schiff base formation.

2.5. Synthesis of 5-membered heterocycles. In 1965, Kmiecik while studying the formation of azobenzene derivatives from nitroaromatics in the presence of CO managed to obtain carbazole in the reaction of 2-nitrobiphenyl with CO in 37% yield (Scheme 28).[106] Later, Cenini *et al*. investigated the role of alkali halides in the synthesis of nitrogen-containing heterocycles by reductive carbonylation of aromatic nitro derivatives catalyzed by $Ru_3(CO)_{12}$ on the example of carbazole formation in up to 88% yields.[107] Furthermore, a new method for carbazole synthesis from 2-nitrobiphenyl derivatives has been developed.[108] On using $Pd(OAc)_2$/1,10-phen as the catalytic system the yield of carbazole reached 97%.

Crotti *et al*. introduced a Ru-catalyzed synthesis of indoles from *o*-nitrostyrenes and CO using metal carbonyls as catalysts (Scheme 29, Table 3, entry 1; for comparison reason Scheme 29 contains only one product).[109,110] Iron, ruthenium and rhodium catalysts were tested. The yields are relatively good (18–75% for different substrates) but high temperatures and CO pressure are required for conducting this process. Later, Bassoli reported ruthenium carbonyl catalyzed indole formation, including trapping of nitroso intermediates using *cis*-cyclooctene as a solvent and investigating the side products.[111] In 1994, Watanabe *et al*. introduced a more effective catalytic system with palladium compounds as metal catalysts for the formation of indoles from 2-nitrostyrenes (entry 2).[112] In this case, the reaction conditions were milder, and the yields of indoles were nearly 50–75%. Later the possible role of arylamine formation in the given reaction has been investigated.[113] Afterwards, Tollari *et al*. applied a new catalytic system to the indole formation reaction (entry 3), and even under relatively mild conditions the yields of indoles reached 99%.[114] Attempts to perform a Rh carbonyl catalyzed process provided maximum indole yields of 85%, but still harsh conditions were required (entry 4).[115]

The concept of palladium-catalyzed indole synthesis from nitroaromatics has been further developed in the work of Söderberg and Shriver, who conducted the reaction at 70 °C, only 4 bar of CO and using $Pd(OAc)_2/PPh_3$ catalytic system.[116] Different *o*-nitrostyrenes were used as substrates, and in some cases indoles in nearly quantitative yields were obtained (Table 3, entry 5). Selenium was also applied as a catalyst; yields varied from 55% to 85% depending on the substrate (entry 6).[117]

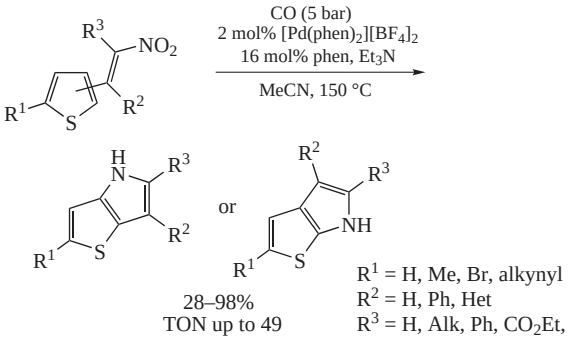
Later, the system was improved, much milder conditions and lower catalyst loadings were achieved, and the substrate scope of the reaction was essentially expanded (see Online Supplementary Materials).[118–132] Palladium mediated indole synthesis was implemented into the preparation of bicyclic thienopyrroles[133]



Scheme 29 Synthesis of 2-phenylindole from 2-nitrostilbene.

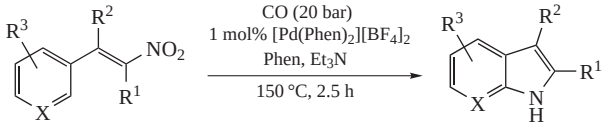
Table 3 Synthesis of indoles (see Scheme 29).

Entry	Catalyst system	CO pressure/bar	*T*/°C	*t*/h	Yield (%)	TON up to	Reference
1	4 mol% $Ru_3(CO)_{12}$	80	220	5	71	18	109
2	5 mol% $PdCl_2(PPh_3)_2$, 50 mol% $SnCl_2$	20	100	1	75	15	112
3	5 mol% $Pd(TMB)_2$, 10 mol% TMPhen	40	180	3	99	20	114
4	2 mol% $[PPN]Rh(CO)_4$, 12 mol% 2-OH-Py	80	170	5	85	42	115
5	6 mol% $Pd(OAc)_2$, 24 mol% PPh_3	4	70	15	100	17	116
6	5 mol% Se, 5 equiv. Et_3N	30	100	15	85	17	117



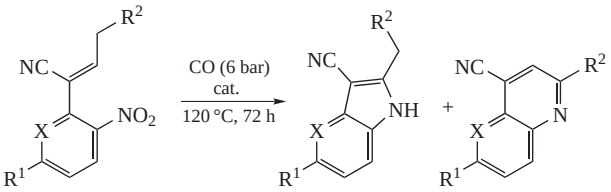
Scheme 30 Synthesis of thienopyrroles.

(Scheme 30). Synthesis of indoles from β-nitrostyrenes in up to 93% yields is also possible (Scheme 31).[134] While studying formation of 3-cyanoindoles in Pd-catalyzed cyclization, Banini *et al*. also discovered formation of substituted quinoline and managed to find conditions to get high yields for both products (Scheme 32).[135]



R^1, R^2 = H, Me, Et, Ph
R^3 = H, Hal, Me, OMe, NR_2
X = CH, N

Scheme 31 Synthesis of indoles from β-nitrostyrenes.

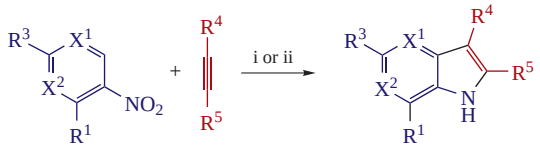


cat. = 10 mol% $Pd(OAc)_2$, 4 equiv. PPh_3	79%	–	
cat. = 12 mol% $Pd(OAc)_2$, 5 equiv. PPh_3, 1.1 equiv. DBU	–	88% TON up to 8	

R^1 = OMe, H R^2 = Alk X = CH, N

Scheme 32 Formation of 3-cyanoindole *vs*. 4-cyanoquinoline.

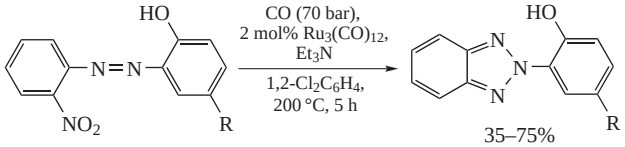
In 2002, Penoni and Nicholas discovered a new catalytic CO-mediated route to indoles using nitroarenes and alkynes as substrates instead of *o*-nitrostyrenes (Scheme 33).[136,137] However, still harsh conditions were needed to drive the reaction while indole yields did not exceed 53%. Palladium catalyst was also effective for such transformation.[138,139]



i, CO (50 bar), 5 mol% $[Cp^*Ru(CO)_2]_2$, benzene, 170 °C, 48 h	23–53% TON up to 11
ii, CO (60 bar), 0.33 mol% $[Pd(phen)_2][BF_4]_2$, 170 °C, 1.5–6 h	45–71% TON up to 215

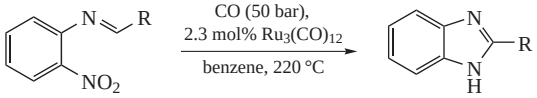
R^1 = H, Me, Cl X^1 = CH, N
R^2 = H, CF_3 X^2 = CR^2, CH, N
R^3 = H, Et_2N, Cl, Br, C(O)OMe, OMe, NO_2, CN, Ph
R^4, R^5 = Alk, Ar, CO_2Me, $SiMe_3$

Scheme 33 Ru-catalyzed synthesis of indoles from nitrobenzenes and alkynes.



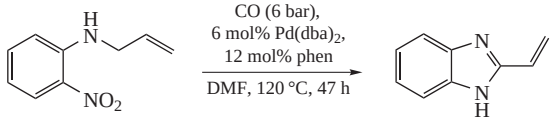
Scheme 34 Synthesis of benzotriazole derivatives.

Ruthenium carbonyl-catalyzed reduction has also been used in the synthesis of benzotriazole (Scheme 34)[140] and benzimidazole (Scheme 35)[141] derivatives in up to 75 and 88% yields, respectively. However, harsh conditions were required.

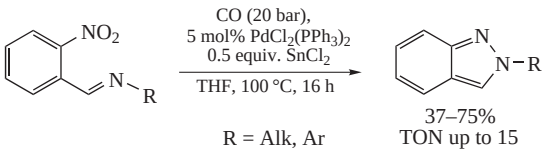


Scheme 35 Ru-catalyzed synthesis of benzimidazole derivatives.

As well as for indole synthesis, the use of palladium catalysts allows one to make the conditions of imidazoles synthesis noticeably milder maintaining good yields (Scheme 36).[142] On using *N*-(2-nitrobenzylidene)amines as substrates, 2*H*-indazole derivatives in a Pd-catalyzed reaction were obtained (Scheme 37).[112,143] For this process, the ionic diamine rhodium complex catalytic system was also applied.[144] The yields of the corresponding 2*H*-indazoles varied from 25 to 85%. Maximum TON for $[Rh(CO)_2(Me_2N\text{-}CH_2CH_2NMe_2)]^+[RhCl_2(CO)_2]^-$ complex reached 17.

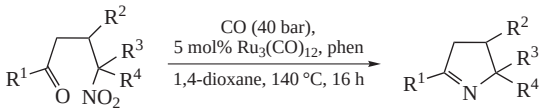


Scheme 36 Pd-catalyzed synthesis of benzimidazole derivatives.



Scheme 37 Synthesis of 2*H*-indazole derivatives.

Intramolecular cyclizations of γ-nitrocarbonyl compounds were reported (Scheme 38).[145] Ruthenium carbonyl was used as a catalyst and comparatively high yields of 1-pyrrolines were obtained.



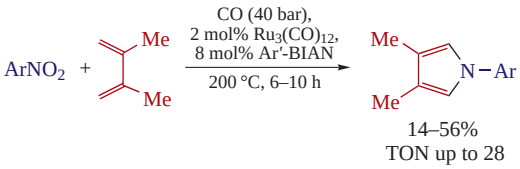
R^1 = Ph, Me R^3 = Me, Et 78–91%
R^2 = H, Ph R^4 = Me, Et, Ph TON up to 18

Scheme 38 Synthesis of 1-pyrrolines.

Synthesis of *N*-arylpyrroles from conjugated dienes was discovered, however it demanded high temperature,[146] a number of side products was detected and the selectivity ranged from medium to low (Scheme 39). A palladium catalyst, namely $[Pd(Phen)_2][BF_4]_2$, was also used for pyrrole synthesis[147] but the selectivity was lower than in the case of ruthenium carbonyl catalysis.

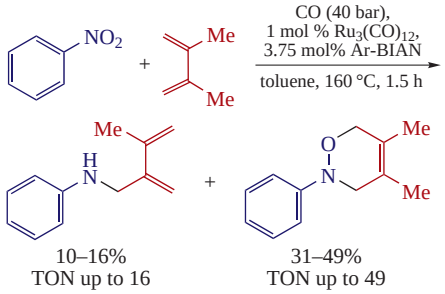
Table 4 Synthesis of quinolines by cyclization of *o*-nitrocinnamic derivatives (see Scheme 41).

Entry	Catalyst system	CO pressure/bar	*T*/°C	*t*/h	Yield (%)	TON up to	Reference
1	4 mol% $Ru_3(CO)_{12}$	80	220	1.5	39	10	109
2	7 mol% $Ru_3(CO)_{12}$, 10% TMphen	70	220	1.5	3	<1	113
3	2 mol% $Rh_6(CO)_{16}$	80	220	1.5	25	13	109
4	5 mol% [PPN]$Rh(CO)_4$, 30 mol% 2-OH-Py	60	170	5	27	5	113
5	5 mol% $Pd(TMB)_2$, 10 mol% TMphen	40	180	3	10	2	113
6	5 mol% $PdCl_2(PPh_3)_2$, 0.5 equiv. $SnCl_2$	20	100	16	34	7	112
7	10 mol% $[Cp^*Fe(CO)_2]_2$	6	150	41	65	6	109, 147, 149



Scheme 39 Synthesis of *N*-arylpyrroles.

2.6. Synthesis of 6-membered heterocycles. Plausible mechanisms of reduction of nitroarenes with carbon monoxide always suggest formation of nitrosoarenes as intermediates. However, they have never been isolated and therefore it was suggested to trap them by the Diels–Alder reaction. Indeed, when 2,3-dimethylbutadiene was added to nitrobenzene under typical reaction conditions, an oxazine was obtained as the main product (Scheme 40).[99] The same type of oxazine was detected in other studies as well.[118,146]



Scheme 40 Formation of oxazines.

The reaction of *o*-nitrocinnamic derivatives with carbon monoxide can lead to quinolines, however, up to date the reported yields are low. The reaction can be catalyzed by rhodium,[109] ruthenium,[109] palladium[112,113] and even iron[109,148,149] complexes, however TON does not exceed 13 (Table 4).

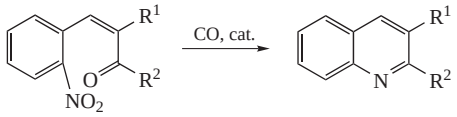
Surprisingly, an intramolecular cyclization of 2-nitrochalcones can lead not only to quinolones but also to *N*-hydroxyquinolones.[150] The use of dry THF is essential for the synthesis of *N*-hydroxy derivatives (Scheme 42).

One of rare examples when six-membered heterocycles are obtained in good yields is the synthesis of 1,2-dihydroquinoxalines and 3,4-dihydroquinoxalinones. Söderberg *et al*. reported reactions of enamines, derived from 2-nitroanilines and α-substituted aldehydes with carbon monoxide (Scheme 43).[151] The disadvantage of the protocol is the low yield with substrates bearing bis-substituted double bond.

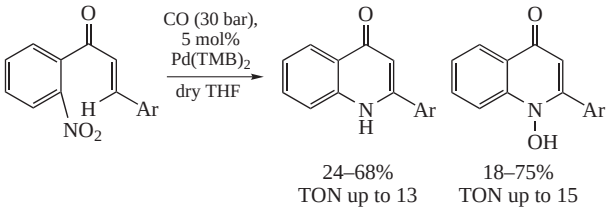
The options for the synthesis of 6-membered heterocycles from nitroarenes are very limited. Quite often such compounds are just byproducts in other syntheses. Even when the chemical yield is high, the turnover numbers do not exceed 20.

Conclusions

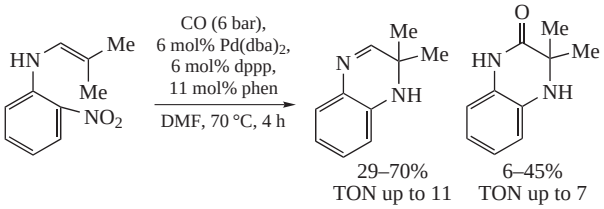
To summarize the results of a large number of studies, it can be noted that reductive addition without an external hydrogen source has been proven to be a powerful strategy which enables access to various useful products. The absence of a hydride reductant provides high selectivity and tolerance to functional and protecting groups including aromatic nitro, cyano, *N*-benzyl, *O*-benzyl, Cbz, trifluoroacetamido, *etc*. which are unstable under classical reductive conditions. Moreover, it leads to the general approaches which were not possible before, *e.g*. to the synthesis of sterically hindered tertiary amines, which was a problem due to sterical hindrance as well as the reduction of starting carbonyl compounds. At the same time, the selectivity of some interesting transformations, such as six member ring synthesis, allylation by alkenes and reactions of amides have not been studied yet in detail. Despite the achievements in the field, there are important aspects of reaction to be explored and improved. We strongly believe that carbon monoxide as well as its surrogates[152–154] represent the best candidates for selective reductive transformations.



Scheme 41 Synthesis of quinolines.



Scheme 42 Synthesis of quinolones and *N*-hydroxyquinolones.



Scheme 43 Synthesis of 1,2-dihydroquinoxalines and 3,4-dihydroquinoxalinones.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.001.

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