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A Review of the Selective Catalytic Reduction of Aromatic Nitro Compounds into Aromatic Amines, Isocyanates, Carbamates, and Ureas Using CO†

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I. Introduction

Carbon monoxide is an important reagent for the functionalization of organic compounds and is used in a wide variety of industrial processes such as carbonylation of alkenes to aldehydes[1] and carboxylic acids[2] and the carbonylation of aryl halides to form aryl carboxylic acids,[3] aldehydes,[4] or amides.[5] The reaction of CO with aryl acetylides is important for the manufacture of branched arylvinyl carboxylates. These intermediates can be utilized as precursors to profens.[6] Furthermore, CO is utilized in the dicarbonylation of acetylenes[7] and in the ring expansion of cyclic ethers (epoxides).[8] Although CO is a toxic gas, it is very attractive industrially due to its low

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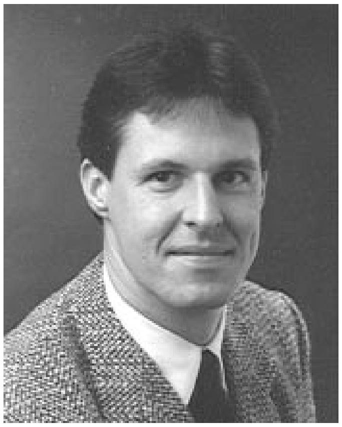

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† Dedicated to Professor Klaus Kühleinm, Director of Research.

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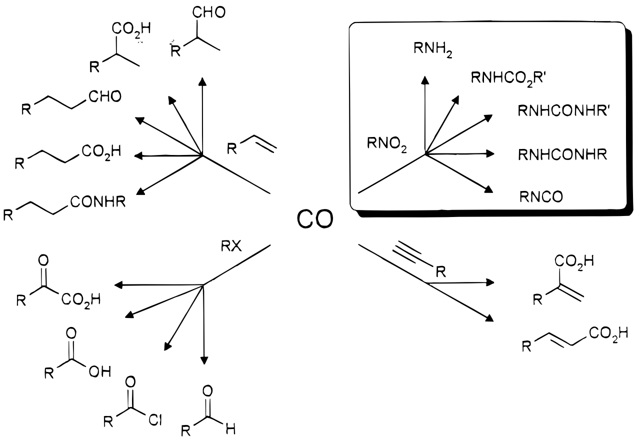
Scheme 1



cost, accessibility, and wide range of applications in the chemical industry. In industry carbon monoxide is utilized in the chemistry of terpolymerization of ethylene and propylene.[9] Carbonylation of methanol to acetic acid is an important reaction of major commercial significance.[10] Also, the carbonylation of isobutylphenylethanol to ibuprofen is economically as well as ecologically advantageous.[11] Finally, CO is important in the reduction of nitro aromatics to aromatic amines, carbamates, ureas, and isocyanates (Scheme 1). Although the use of CO as a reductant had been in the past confined to few reactions, its use in organic synthesis, especially in the reductive carbonylation of nitro aromatics and the oxidative carbonylation of aromatic amines, has increased dramatically. Since the discovery of CO-induced reduction of nitro groups, there has been a wide spread increase of interest in the application and mechanistic understanding of this reaction. In a major review[12] published in 1988 it was noted, that "...in practice no studies of the mechanism of N-carbonylation of aromatic nitro compounds with alcohols leading to carbamates have been carried out." This review clearly shows a major change since that publication. Indeed, metal-catalyzed reductive carbonylation of nitro aromatics using CO as reducing agent has been in the past 10 years the subject of intense investigation both in academia and in the chemical industry. Several articles and reviews have covered the subject up to the late 1980s.[13−15] We will concentrate on more recent literature, but sometimes older data will be used to establish an understanding of these reactions.

II. Synthesis of Isocyanates

II.A. Introductory Remarks

Isocyanates, such as methylenediphenyl isocyanate (MDI) or toluene diisocyanate (TDI), have achieved great commercial importance in the manufacture of polyurethanes. Furthermore, isocyanates can be used as precursors in the synthesis of herbicides. The conventional synthesis consists of hydrogenation of a nitro aromatic and subsequent phosgenation of the resulting aromatic amine (route 1, Figure 1).

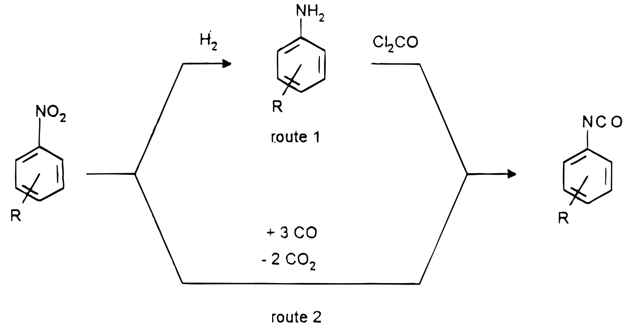


Figure 1.

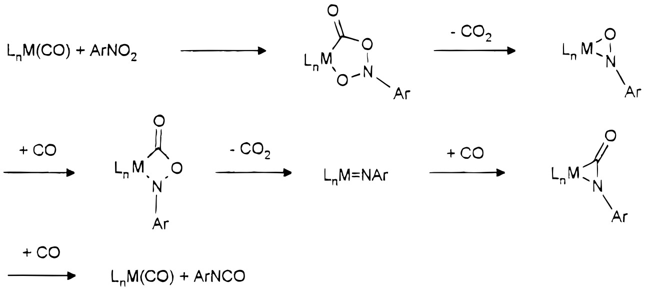


Figure 2.

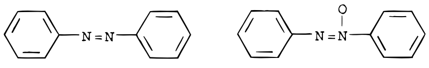


Figure 3.

Since extremely toxic phosgene is used and large amounts of corrosive HCl are produced as a side product in the conversion of aromatic amine to isocyanate, many efforts have been made to develop an alternative, phosgene-free process. In 1967 Hardy and Bennett[16] reported first the conversion of aromatic nitro compounds to isocyanates by CO (route 2, Figure 1). This reductive carbonylation is a thermodynamically favorable, highly exothermic process. For instance, the conversion of nitrobenzene to phenyl isocyanate has a ΔH_r value of approximately −128.7 kcal/mol,[17] yet the reaction does not proceed in the absence of a catalyst system.

In addition to group 8−10 metal compounds, sulfur, selenium, or tellurium could also be used, but the latter have the problem that small but detectable amounts of the highly toxic catalyst are present in the final product.[18,19] Therefore, this review will concentrate on the group 8−10 metal compounds.

II.B. Mechanism

The mechanism generally accepted for the reaction catalyzed in the homogeneous phase is based on the following steps.[20] Initially, in the presence of CO and the catalyst, the nitro compound generates a metallacycle. This intermediate undergoes decarboxylation, leaving the nitroso group η^2-bound to the metal. The subsequent insertion of CO followed by decarboxylation gives a nitrene species as key intermediate, which can be carbonylated to give the isocyanate (Figure 2).

The nitrene species can also react with a nitroso compound or another nitrene intermediate, yielding azoxy or azo compounds as side products (Figure 3).

II.C. Catalyst Systems

The carbonylation of nitro compounds to give the corresponding isocyanates has been carried out mainly by using palladium and rhodium as catalyst.[21,22] The

Table 1. Reductive Carbonylation of Nitrobenzene to Phenyl Isocyanate with Palladium Catalysts in the Presence of TMphen[a] [23]

entry	catalyst	acid	% conversion	% selectivity
1	Pd/Al_2O_3 + TMphen	TMBA	43	53
2	$Pd(TMB)_2$ + TMphen	TMBA	42	82
3	$Pd(OAc)_2$ + TMphen	TMBA	42	74
4	$Pd(OAc)_2$ + TMphen	AcOH	24	9

[a] Reaction conditions: $T = 180$ °C, $p = 40$ bar, ligand/Pd = 2, acid/Pd = 24.

catalyst can be applied in a homogeneous or a heterogeneous system, but it has been proposed that the catalyst is leached from the support and reacts homogeneously.[23] Oxide or chloride promotors such as $FeCl_3$, $MoCl_5$, V_2O_5, and Fe_2O_3 have been found to be very effective and to permit less drastic reaction conditions. The promoting effect is not well-understood, but it is assumed that Lewis acids could promote the insertion of CO into the metal−nitrogen bond, as they do for the insertion of CO into metal−carbon bonds. Another explanation is the activation of the nitro group by coordination, favoring deoxygenation.[14]

It is also possible to activate the noble metal catalyst with nitrogen-containing ligands such as pyridine or quinoline. Metal salts, complexes, or supported metals can be used as catalyst precursors which are converted under the reaction conditions in the presence of a ligand to a catalytically active complex of unknown composition.[24] Substituents of the ligand influence the activity and selectivity of the catalyst. In the case of $Pdpy_2Cl_2$, electron-donating alkyl substituents not in the α-position of the pyridine ring increase the degree of conversion and yield, whereas electron-withdrawing substituents in the *β*-position and bulky substituents have a negative effect on the reaction.[25,26]

Recently bidentate ligands, in the presence of trimethylbenzoic acid (TMBA) as cocatalyst, have been used in this reaction.[23] In this case it was possible to work with much lower CO pressure, in the range of 20−50 bar. In analogy to pyridine ligands, substituents in the α-position have a negative effect, whereas electron-donating ligands not in the α-position have a positive effect on this reaction. The catalytic activity was observed to increase in the order 2,9-dimethyl-1,10-phenanthroline < 2,2′-bipyridine (bipy) < 1,10-phenanthroline (phen) < 3,4,7,8-tetramethyl-1,10-phenanthroline (TMphen). To obtain the best results the ligand/Pd ratio should be 2−3 and an excess of TMBA is essential.

Pd/Al_2O_3 can be used as Pd source (entry 1, Table 1), but it shows poorer selectivity than Pd(II) salts (entries 2 and 3). The $Pd(OAc)_2$/TMphen system works very well if an excess of TMBA is present, but it is severely deactivated when excess AcOH is employed instead of TMBA (entries 3 and 4). It is assumed that a sterically hindered acid is necessary. However, according to Drent it is also possible to use p-toluenesulfonic acid.[27]

Next to the production of phenyl isocyanate as precursor to MDI, the production of TDI is also very interesting. In this case two nitro groups have to be converted to the isocyanate moiety, which complicates the reaction, since the presence of one NCO group on the aromatic ring slows the reaction of the second (Figure 4).

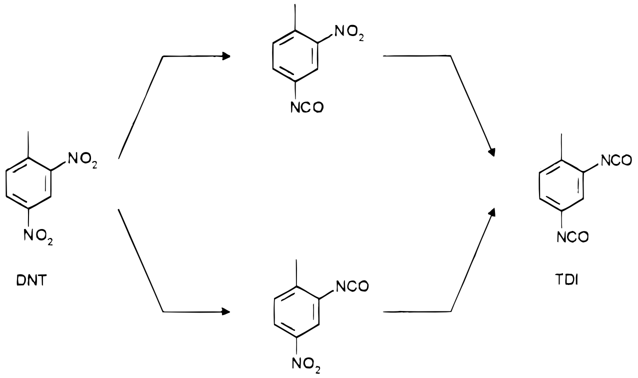


Figure 4.

The catalyst most often used in this reaction is PdL_2Cl_2 (L = pyridine, isoquinoline) in the presence of a cocatalyst such as metal oxides or chlorides.[28,29] Ugo et al. found during the investigation of the stability of a $Pd(isoquinoline)_2Cl_2$ catalyst that cocatalysts such as $Fe_2(MoO_4)_3$ or Fe_2O_3/MoO_3 activate the palladium complex by reduction of Pd(II) to a low oxidation state palladium. It was suggested that the catalytic entity is a soluble zero-valent complex, which is stabilized by the nitro compound and the ligands.[29] The activity, selectivity, and stability of the catalytic system are directly related to the nature of the coordination sphere of the zero-valent palladium atom. If it is too ligand deficient, deactivation to metal quickly occurs, but if the coordination sphere is too firmly filled, the reaction and the synthesis of isocyanates are completely inhibited since no interaction with the nitro compound is possible.

Since the carbonylation to the monoisocyanato derivatives is easier and can be realized at lower temperatures, the process can be carried out in two separate stages. The first stage occurs at 150 °C, producing mainly monoisocyanato derivatives, which are converted in a second stage at 200 °C to TDI. This procedure has the advantage of milder reaction conditions, avoiding the oligomerization or polymerization of isocyanates. These undesired side reactions can also be avoided by using high catalyst concentrations, providing high reaction rates. In this case the isocyanate products formed are exposed for shorter contact times and the side reactions are minimized.

Under optimized reaction conditions with a $Pd(isoquinoline)_2Cl_2/Fe_2(MoO_4)_3$ catalyst ($p = 200$ atm, DNT/Pd = 14), the yield of TDI amounts to 68%. Recently a very similar catalyst system consisting of $Pd(quinoline)_2Cl_2$, bis(2,4-pentanedionate)oxovanadium, and phosphoryl chloride was reported to yield 65% TDI. The advantage of this catalyst system is the ability to recover 91% of the catalyst by precipitation, reducing the disadvantage of using high levels of Pd to DNT.[30] Because of the instability of isocyanates under the reaction conditions, the high level of Pd to nitro compound, and the often low yields of isocyanates, the emphasis in the present literature on reductive carbonylations lies on the generation of *N*-phenylcarbamates, which can be used as precursors for MDI and TDI.

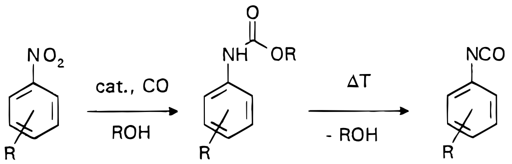


Figure 5.

III. Synthesis of Carbamates

III.A. Introductory Remarks

N-Phenylcarbamates are interesting precursors of the corresponding isocyanates, which themselves are important intermediates in the production of polyurethanes. In most cases reductive carbonylation of nitro aromatics to carbamates, which is an even more exothermic reaction than the one to isocyanates, is catalyzed by palladium, ruthenium, and to a lesser extent rhodium. Furthermore platinum,[31] iridium,[32] and iron[33] have also been reported to be active in this reaction. Conversion of carbamates to isocyanates can be achieved by thermal treatment at high temperatures[34] (Figure 5), but often this reaction is accompanied by side reactions such as Grob fragmentation[35] or, in the case of aromatic carbamates based on ethanol, by a thermally allowed electrocyclic process (cis-elimination), which leads to amines, olefins, and carbon dioxide.

III.B. Mechanism

For the reductive carbonylation of nitro compounds carried out in alcohol, it might generally be considered that the carbamate is formed by reaction of ArNCO with ROH outside the coordination sphere of the metal.[20] However, Cenini has found that in the case of $Ru_3(CO)_{12}$ with NEt_4Cl as cocatalyst the alcohol should participate in the catalytic cycle, since when it was absent, practically no isocyanate was obtained.[36] He suggests that another mechanism could be involved (Figure 6).

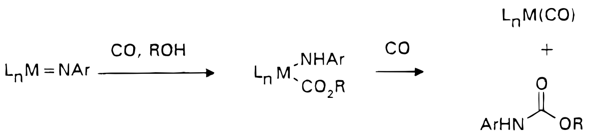


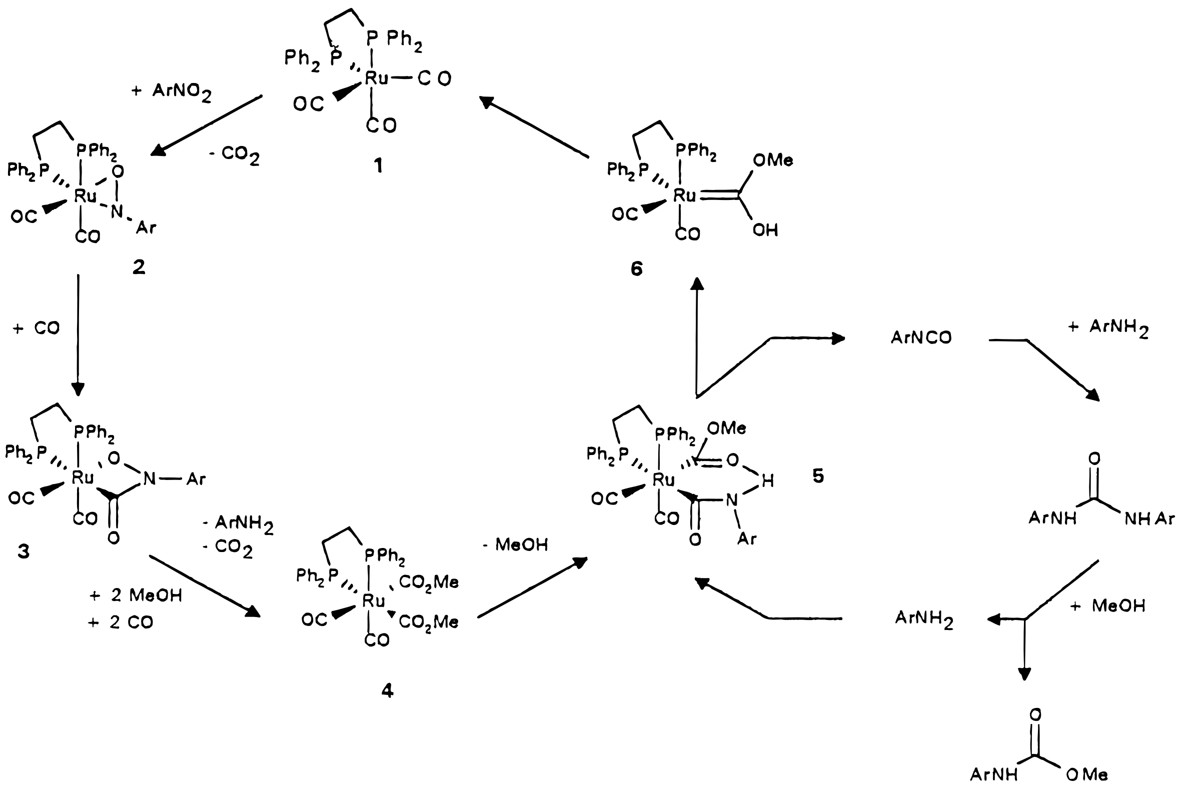
Figure 6.

As described in the mechanism of isocyanate formation, a nitrene complex is the key intermediate. This complex may form an alkoxycarbonyl species by alkoxide attack on a carbonyl, which couples with the nitrene ligand after protonation to yield the carbamate product.

Recently several papers were published by Gladfelter and Cenini giving more insight into the mechanism of the catalytic cycle of rhodium and ruthenium catalysts. Gladfelter has proposed a mechanism using $Ru(dppe)(CO)_3$ (**1**) (dppe = bis(diphenylphosphino)ethane) as a catalyst, in which aromatic amine is suggested as an intermediate.

He showed that in the first step the nitro aromatics are converted to $Ru(dppe)(CO)_2(\eta^2\text{-NOAr})$ (**2**)[37] via a one-electron transfer process (Scheme 2).[38] This intermediate might undergo a CO insertion to form the four-membered metallacyclic intermediate Ru(dppe)$(CO)_2$[C(O)N(Ar)O] (**3**)[39] which reacts quantitatively with MeOH to generate the bis(methoxycarbonyl) complex $Ru(dppe)(CO)_2[C(O)OMe]_2$ (**4**)[39] and aromatic amine. This complex and aromatic amine are in equilibrium with $Ru(dppe)(CO)_2[C(O)OMe]$-[C(O)NHAr] (**5**).[40] The C−N bond formation involves

Scheme 2

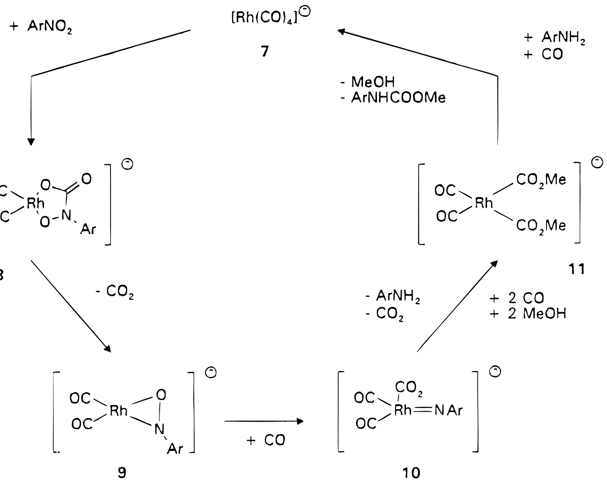


nucleophilic attack of $ArNH_2$, probably on a metal carbonyl and not on a methoxycarbonyl ligand.[41] This intermediate undergoes unimolecular elimination of aryl isocyanate, which is rapidly trapped by aromatic amine to give *N*,*N*′-diphenylurea. In the product forming step *N*,*N*′-diarylurea reacts with MeOH to yield methyl *N*-arylcarbamate.

Gladfelter could isolate and fully characterize complexes **1**−**4**, whereas complex **5** has been observed but neither fully characterized nor isolated.

Very similar results were obtained by Cenini using $[(PPh_3)_2N][Rh(CO)_4]$ (**7**)[42−45] as catalyst. A simplified reaction scheme of his proposed mechanism is shown in Scheme 3.

Scheme 3



He could also show that an electron transfer process is involved in the reaction of the nitro aromatic compound and the catalyst.[45] As a first intermediate a complex with $[Rh(CO)_2ON(Ar)C(O)O]^-$ (**8**) as anion could be isolated,[44] which reacts via a nitroso complex **9** (in analogy to **2**) to a nitrene complex, $[Rh(CO)(CO_2)NAr]$ (**10**). The existence of this species was suggested by trapping experiments with nitroso compounds.[45] In analogy to Gladfelter's results, the alkoxycarbonyl complex **11** and aromatic amine are proposed as intermediates, which react to give carbamate and starting material **7**.

In the field of mononuclear catalysts another metallacyclic complex of palladium, Pd(phen)[C(O)-ON(Ar)C(O)] (phen = phenanthroline) (**12**) (Figure 7), has been previously isolated and shown to be an intermediate in the catalytic cycle.[21] Recently van Leeuwen found that the presence of aniline caused a large increase of catalytic activity of $Pd(phen)_2(OTf)_2$,[46] indicating that aromatic amine is an intermediate. So in the case of palladium, it can also be suggested that the mechanism is similar to those of ruthenium and rhodium.

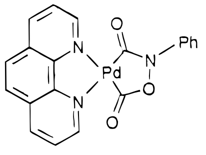


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Figure 7.

III.C. Catalyst Systems for Carbamate Synthesis

III.C.1. Ruthenium Catalysts

Ruthenium carbonyl complexes such as $Ru_3(CO)_{12}$ or $Ru(CO)_3(PPh_3)_2$ are efficient homogeneous catalysts in the reductive carbonylation of aromatic nitro compounds to carbamates if additives such as alkylammonium salts,[47,36] chelating ligands,[48] or anilines[49] are used.

Cenini investigated several ammonium salts in this reaction and found that activity and selectivity are strongly influenced not only by the nature of the anion but also of the cation. The best combination is NEt_4Cl, giving carbamate with 93% selectivity and 100% conversion. The influence of halides on this reaction was investigated by Geoffroy,[50] demonstrating that halides promote both the formation of nitrene ligands from nitrosobenzene, but not significantly from nitrobenzene, and the carbonylation of the nitrene.

The carbamate formation is also influenced by the alcohol used. According to Cenini, methanol is more selective than ethanol and phenol. Cheng showed that an alcohol such as *tert*-butanol, which would not undergo dehydrogenation under reaction conditions, is more selective than methanol.[43] However, it was found that *tert*-butanol is less reactive than methanol.

The $Ru_3(CO)_{12}/NEt_4Cl$ catalyst tolerates a variety of substituents such as chloro, alkyl, trifluoromethyl, or carbomethoxy groups on the aromatic nucleus of the nitro compound. Good yields (73−88%) were always obtained in the synthesis of these carbamates. The reactivity of the catalyst decreases when using dinitrotoluene as a substrate due to catalyst decomposition, and selectivity to the biscarbamate amounts to only 45−50%.[36]

It was found that the activity of $Ru_3(CO)_{12}$ in this reaction can also be notably increased by adding neutral chelating ligands such as dppm (bis(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)-propane), 2,2′-bipyridine, and phenanthroline.[48] The most active ligand was 2,2′-bipyridine, yielding 82% of the carbamate.

An interesting process was developed by Catalytica and Haldor-Topsoe[49] using $Ru_3(CO)_{12}$ as catalyst and a mixture of nitrobenzene and aniline. The chemistry proposed for this reaction is interesting, involving first the oxidative carbonylation of aniline, as shown in eq 1. For this reaction to proceed thermodynamically, the hydrogen atoms produced must be consumed immediately on formation. This is accomplished by reaction with nitrobenzene and CO to produce aniline and carbon dioxide according to eq 2.

$$PhNH_2 + CO + CH_3OH \rightarrow PhNHCO_2CH_3 + 2H \quad (1)$$

$$PhNO_2 + 2CO + 2H \rightarrow PhNH_2 + 2CO_2 \quad (2)$$

$$PhNO_2 + 3CO + CH_3OH \rightarrow PhNHCO_2CH_3 + 2CO_2 \quad (3)$$

The net result obtained by combining the two equations is the combination of nitrobenzene with carbon monoxide and methanol to give methyl *N*-phenylcarbamate and carbon dioxide according to eq 3. The aniline should be present in the reaction mixture at the end in exactly the same concentration as it was at the beginning, provided that the first two reactions proceed according to the indicated stoichiometry. Theoretically, only a catalytic amount of aniline should be required, but high concentrations of aniline are prefered, because it was observed to enhance the rate of the reaction and the selectivity to the desired product. Another mechanism described involves urea formation. Here, aniline reacts with carbon monoxide to provide urea and two atoms of hydrogen. The reaction of nitrobenzene with carbon monoxide and the hydrogen yields aniline and carbon dioxide. The transformation of diphenylurea with MeOH provides carbamate and aniline. Again, the net result is that nitrobenzene, carbon monoxide, and alcohol yield the carbamate and carbon dioxide as overall reaction products.

$$2PhNH_2 + CO \rightarrow PhNHCONHPh + 2H \quad (4)$$

$$PhNO_2 + 2CO + 2H \rightarrow PhNH_2 + 2CO_2 \quad (5)$$

$$PhNHCONHPh + CH_3OH \rightarrow PhNHCO_2CH_3 + PhNH_2 \quad (6)$$

$$PhNO_2 + 3CO + CH_3OH \rightarrow PhNHCO_2CH_3 + 2CO_2 \quad (7)$$

In one example a mixture of nitrobenzene and aniline in a 2:1 ratio dissolved in methanol was converted to carbamate with CO and $Ru_3(CO)_{12}$ as catalyst, giving 100% conversion and 95% selectivity. The amount of aniline increased by only 4%. Taqui Khan et al. showed that Ru(III) complexes are also active in the reductive carbonylation of nitro aromatics.[51] They investigated compounds **12**−**16** (Figure 8) at 15 atm in the temperature range of 160−200 °C, generating exclusively carbamates. The activity of the complexes decreased in the order [Ru(saloph)Cl_2] (**12**) ≫ [Ru(salen)Cl_2] (**13**) > [Ru(pic-en)Cl_2]Cl (**14**) > [Ru(pic-opd)Cl_2]Cl (**15**). Complex **16** was completely inactive even after 12 h of contact time.

The order of activity clearly shows that the complexes with two coordinated N- and two coordinated O-atoms ("N_2O_2") are more active than those with four coordinated N-atoms ("N_4"), while the system with five coordinated N-atoms ("N_5") is catalytically inactive. The latter result can be explained by the necessity of the presence of labile *trans*-chlorides in the coordination sphere of the metal ion, which can provide vacant coordination sites for the coordination of CO and the nitro compound. Complexes with "N_2O_2" coordination on Schiff bases, which form more flexible complexes than a rigid "N_4" system, allow rearrangement in the coordination sphere of the metal ion. This explains the higher catalytic activity of the "N_2O_2" Schiff bases over the "N_4" systems. The exchange of the salicylaldehyde unit in complexes **12**, **13**, and **16** against naphthaldehyde units showed, on one hand, the same order of catalytic activities, but on the other hand, the activity was much lower.[52] This can be explained by steric hinderance at the equatorial position.

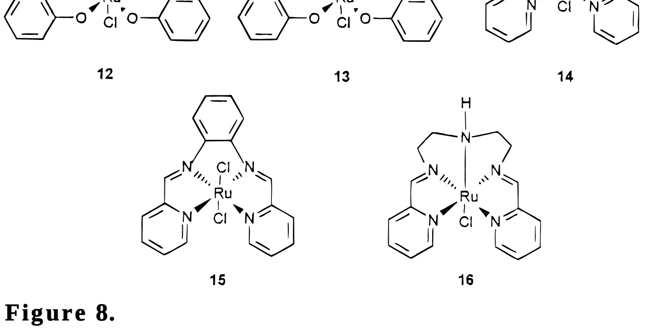


Figure 8.

Also orthometalated Ru(II) complexes of the type $[RuL(CO)_2Cl]_2$ (LH, e.g. 2-phenylpyridine) have been applied to this reaction. It turned out that mild coordinating solvents and basic cocatalysts are necessary to guarantee yields up to 80% of carbamate.[53] Nonpolar solvents probably cannot break the dinuclear complex to the corresponding monomer, while in a strong coordinating medium the corresponding solvent adducts do not allow the formation of a metal−substrate complex. The activity order of the basic cocatalysts was consistent with their corresponding basicity, and alkoxides such as NaOMe were found to be the most effective. Acidic cocatalysts on the other hand only increased the formation of undesired aniline.

III.C.2. Palladium Catalysts

III.C.2.1. Influence of Ligands, Counterions, and Cocatalysts. In the reductive carbonylation of nitrobenzenes, palladium is often applied as catalyst in homogeneous as well as in heterogeneous systems. Although heterogeneous catalysts such as Pd/Al_2O_3 and Pd/C[54] were conceived and designed to provide a system with the ease of filterability and reusability for several cycles, they actually form homogeneous complex species in situ. This happens by leaching of the noble metal from the support. This effect is responsible for the high activity and selectivity in the reductive carbonylation of nitrobenzene.[23] Montmorillonite bipyridinylpalladium(II) acetate,[55] which is an anchored Pd-catalyst supported on montmorillonite, has recently been used in reductive carbonylation. By activating this system with $Ru_3(CO)_{12}$ in the presence of bipyridine, it was possible to generate even diurethanes in good yields.[56] When using $FeCl_3$/pyridine as cocatalyst, Chaudari et al. found that the catalyst could be reused successfully for seven cycles with consistent activity.[57]

In the case of homogeneous catalysis, most of the early reported catalytic systems require corrosive Lewis acids and/or a base such as pyridine or triethylamine in excess amounts.[58] Better results were obtained using bidentate nitrogen or phosphorus ligands with cocatalysts in the absence of Cl^- anions. These systems were investigated very intensively with regard to the electron-donating capacity of the ligand and the nature of the cocatalysts and counterions in cationic complexes. Mestroni[59] and Drent[60] first reported that palladium catalysts with bindentate ligands such as bipyridyl or phenanthroline in

Table 2. Influence of Bidentate Ligands on the Reductive Carbonylation of Nitro Aromatics to Carbamates[a] [61]

ligand	% conversion	% selectivity
bipy	15	85
phen	72	97
TMphen	99	98

[a] Reaction conditions: $[PhNO_2]/[Pd] = 250$; $T = 250$ °C; $p(CO) = 40$ atm.

Table 3. Influence of Substituted Bipyridine and Phenanthroline Ligands on the Reductive Carbonylation of Nitro Aromatics to Carbamates[a] [63,64]

entry	catalyst	TOF (mol/mol per h)
1	$Pd(Cl_2\text{-bipy})_2(OTf)_2$	0
2	$Pd(bipy)_2(OTf)_2$	75
3	$Pd(Me_2\text{-bipy})_2(OTf)_2$	60
4	$Pd(MeO_2\text{-bipy})_2(OTf)_2$	55
5	$Pd((Me_2N)_2\text{-bipy})_2(OTf)_2$	57
6	$Pd(Cl_2\text{-phen})_2(OTf)_2$	11
7	$Pd(phen)_2(OTf)_2$	234
8	$Pd(Me_2\text{-phen})_2(OTf)_2$	311
9	$Pd(MeO_2\text{-phen})_2(OTf)_2$	179
10	$Pd((Me_2N)_2\text{-phen})_2(OTf)_2$	95

[a] Reaction conditions: $T = 135$ °C, $p(CO) = 80$ bar.

the presence of a Brönsted acid are more active in the reductive carbonylation of nitro aromatics than those with monodentate ligands. For a $[Pd(\text{bidentate ligand})_2][PF_6]]_2$ catalyst system the catalytic activity increases in the series bipy < phen < TMphen according to the donating capacities of the ligands[61] (Table 2). The same tendency was observed using palladium on charcoal as catalyst precursor,[54] which is not surprising since the palladium has been shown to leach from the support, generating a homogeneous catalyst.

The relatively high activity of the 1,10-phenanthroline ligands, which is described in many papers,[61,62,64,66] is probably caused by the rigidity of these ligands. In the more flexible 2,2′-bipyridine ligand, on the other hand, free rotation around the linking bond is possible. This results in lower complexation constants for this ligand. Van Leeuwen et al. have reported the influence of electron-donating and electron-withdrawing substituents of bipyridine[63] and phenanthroline[64] ligands on the catalytic activity. As can be seen in Table 3 both ligand systems show no or only very low activity in the case of electron-withdrawing substituents (entries 1 and 6). Bipyridyl ligands with a donating capacity higher than that of 2,2′-bipyridine apparently do not increase the overall conversion of the substrate. Only small differences were found between the different substituted ligands (entries 2−5).

Replacement of the bipyridyl ligands with 4,7-disubstitited-1,10-phenanthroline ligands (entries 6−10) yielded more active catalysts. In this case the donating substituents led to larger differences in catalytic activity, and an optimum was found for the $Pd(Me_2\text{-phen})_2(OTf)_2$ complex with a TOF (turnover frequency) of 311 mol/mol per h.

Besides the ligand effect, the anion also seems to play an important role. Table 4 points out that catalysts with noncoordinating anions such as PF_6^- and BF_4^- show almost the same activity and selectivity, whereas replacement with coordinating anions such as chloride or acetate causes a sharp loss of both activity and selectivity.[61] The triflate anion was found to be even more active in the presence of Me_2-phen as ligand.[64] This might have to do with the very weak coordination of the triflate anions compared to the noncoordinating BF_4 anions, indicating a subtle balance between the donating capacity of the ligand and the degree of coordination of the anion.

Table 4. Influence of Counterions in Pd Complexes on the Reductive Carbonylation of Nitro Aromatics to Carbamates[a] [61]

catalyst	% conversion to nitrobenzene	% selectivity
$[Pd(TMphen)_2][PF_6]_2$	100	97
$[Pd(TMphen)_2][BF_4]_2$	100	94
$[Pd(TMphen)Cl_2] + TMphen$	13	75
$[Pd(TMphen)(OAc)_2] + TMphen$	30	41

[a] Reaction conditions: $T = 180$ °C, $p(CO) = 40$ atm.

In principle it is possible to generate palladium catalysts in situ from $Pd(OAc)_2$ and ligand, but in this case strong acids like p-toluenesulfonic acid are required as cocatalyst.[60,64] Strong acids are probably needed to replace the coordinating acetate anions by noncoordinating anions like tosylates. It has also been demonstrated in the case of $Pd(phen)_2(OTf)_2$ as catalyst that the use of Brönsted acids such as benzoic acid increases the activity by the factor of 1.5 and enhances the selectivity from 84 to 94%.[65] Although the increase of the activity and selectivity depends on the amount of acidic cocatalyst present, no correlation could be found with the pK_a value of the acid. The accelerating effect of the cocatalyst is explained by protonation of the amide oxygen or nitrogen atom in metallacycle **12** (Figure 7) causing ring opening.[21]

The catalytic effectiveness of Pd(II)−phenanthroline catalyst systems can also be significantly improved by using $Ce(SO_4)_2$ and V_2O_5 as promotors.[66] The promoting effect of $Ce(SO_4)_2$ is explained by a redox cycle involving Ce(III/IV) cations. At the high oxidation state, Ce(IV) oxidizes inactive Pd(0) species to Pd(II), while at low oxidation state, Ce(III) assists the deoxygenation of nitrobenzene with reoxidation of Ce(III) to Ce(IV).

Besides bidentate nitrogen ligands, bidentate phosphorus ligands can also be used, although only a few examples of Pd/phosphine catalyst systems are known for this reaction. Alper has used a $Pd(dppp)Cl_2/K_2CO_3$ catalyst system for the conversion of several nitro aromatics,[67] whereas Drent used a system consisting of $Pd(OAc)_2$, dppp, and 2,4,6-trimethylbenzoic acid.[60] Van Leeuwen tested a series of phosphorus ligands, from which dppp was found to be the best.[68] In all cases the catalysts were less active and selective than the above mentioned systems with nitrogen ligands. The reason for this was shown to be the oxidation of the phosphine ligand by the nitro compound, yielding phosphine oxide, which is inactive.[68] Recently a new type of homogeneous palladium catalyst has been applied in which the addition of donor ligands is made unnecessary by the presence of a heteropoly acid (HPA).[69−71] The

Table 5. Reductive Carbonylation of Substituted Nitrobenzene with $Pd(phen)_2(OTf)_2$ as Catalyst[a] [46]

entry	substituent	$E_{1/2}$ (V)	TOF (mol/mol per h)	% selectivity
1	*p*-F_3C	−0.66	241	59
2	H	−0.81	234	84
3	*p*-Me	−0.82	226	86
4	*p*-MeO	−0.85	58	100
5	*p*-Me_2N	−0.91	37	100
6	*o*-F_3C	−0.76	47	46
7	*o*-Me	−0.88	199	42
8	*o*-i-Pr		197	31
9	*o*-t-Bu		197	13
10	*p*-CN		117	31
11	*p*-C(O)Me		365	55
12	*p*-C(O)OEt		157	65
13	*p*-OH		157	100
14	*p*-C(O)OH		365	94
15	*p*-NO_2		73	86

[a] Reaction conditions: $T = 135$ °C, $p(CO) = 60$ atm.

optimum catalyst was found to be a $PdCl_2/H_3PMo_{12}O_{40}$ system, which gave a TOF of 28 mol/mol per h and a selectivity toward the desired carbamate of 97%.[69] Initially the HPA was believed to act as an oxidizing agent in the catalytic cycle. Pd(0) intermediates, which might be formed during the conversion of nitrobenzene, need to be reoxidized to the original Pd(II) compounds by the heteropoly acid, and nitrobenzene was supposed to reoxidize the reduced HPA species.[71] However, the fact that nitrobenzene turned out to be unable to reoxidize the reduced HPA species weakens this argument. More likely, the reduced heteropoly anion should be considered as a large inorganic ligand that can interact with the Pd(II) center in a manner that is comparable to the bidentate nitrogen or phosphorus ligands.[70]

III.C.2.2. Influence of the Nitro Compound. Most studies on the palladium-catalyzed carbonylation of aromatic nitro compounds have been performed with nitrobenzene as model substrate for the sake of simplicity and the fact that it can be used as precursor of MDI, which is of industrial interest. Recently the influence of electronic as well as steric properties and the resistance of several functional groups on the nitro substrate have been investigated with $Pd(phen)_2(OTf)_2$ as catalyst.[46] The influence of the electronic properties of the substrate on the catalytic activity and selectivity was studied by introduction of various electron-withdrawing or electron-donating substituents at the para-position of nitrobenzene. The donating capacity of the substituents increases in the order $F_3C < H < Me < MeO < Me_2N$, which is in good agreement with the oxidizing capacities (determined as half-wave potentials, $E_{1/2}$, entries 1−5, Table 5) of these substrates. From the TOF's listed in Table 5 it can be seen that the catalytic activity is reduced going from electron-withdrawing to electron-donating substituents. As the activity decreases in this row, this might imply that the substrate is needed for the reoxidation of Pd(0) to Pd(II) at some stage in the catalytic cycle. Apparently $E_{1/2}$ must be above a certain, value as can be seen from the sharp decrease from *p*-methylnitrobenzene to *p*-nitroanisol (entries 3 and 4). Above this minimum level, a further increase of the oxidizing capacity only leads to relatively small enhancement of the activity. As the activity decreased, the reaction became more and more selective toward the carbamate under the influence of electron-donating substituents in the substrate. In the case of electron-withdrawing substituents, the azoxybenzene and azobenzene derivatives became important side products as a result of a rapid formation of the nitroso and nitrene derivatives.

Introduction of steric hinderance at the ortho-position caused a decrease in the activity (entries 6 and 7). Yet, if the substituents were really bulky, like a *tert*-butyl or an isopropyl group, reasonably fast reactions were again obtained, due to the formation of an interesting class of side products. In this side reaction additional methoxy substituents were introduced to the aryl ring of the generated products. In the case of an *o*-*tert*-butyl substituent the methyl *N*-(methoxyaryl)carbamate became the main product (entry 9).

The cyano, carbonyl, alkoxycarbonyl, hydroxyl, and hydroxycarbonyl groups (entries 10−14) have been shown to be resistant to the reaction conditions needed for the reductive carbonylation of the nitro group, while in the case of 4-nitrobenzaldehyde and 4-nitrobenzyl chloride, no carbamate or any common side product was detected. Especially with 4-nitrobenzoic acid, a remarkably high activity and selectivity was found. This can be explained by the fact that Brönsted acids have a positive effect on activity and selectivity.[65] So 4-nitrobenzoic acid acted as substrate as well as its own cocatalyst. Also dinitro compounds such as 1,4-dinitrobenzene could be converted to the dicarbamate with high selectivities and acceptable TOF's (entry 15).[72]

III.C.3. Rhodium Catalysts

Rhodium catalysts have been applied less often to the reductive carbonylation of nitrobenzene than ruthenium and palladium catalysts. Cenini showed that $Rh_6(CO)_{16}$ is catalytically active in this reaction at 60 atm and 170 °C, if chelating ligands are present.[48] In analogy to the palladium catalysts, bidentate nitrogen ligands such as bipyridine are superior to bidentate phosphorus ligands such as dppe. Pyridine as monodentate ligand did not show any selectivity toward carbamate.[45] These results are in contrast to those obtained when using $[(PPh_3)_2N][Rh(CO)_4]$ as catalyst. In this case pyridine, *N*-methylimidazole and triethylamine also enhanced the reaction rate, indicating that the nitrogen compounds are apparently acting only as a base and that their chelating nature is not influential.[45] Instead of the monomeric $[Rh(CO)_4]^-$, the rhodium cluster $[Rh_5(CO)_{15}]^-$ and bimetallic clusters of the general formula $[(PPh_3)_2N][MRh_4(CO)_{15}]$ (M = Fe, Ru, Os) were also tested, but they were found to be less suitable.[42] Interestingly $Rh(py)_3Cl_3$ and $Rh(CO)Cl(PPh_3)_2$ as catalyst were found to be much more active if they were supported on alumina or ZSM-5 than under homogeneous conditions.[73]

Dicarbonylacetylacetonatorhodium and $Rh_6(CO)_{16}$ can be used as catalysts in the presence of a mixture of nitrobenzene and aniline[49g] in the same way as $Ru_3(CO)_{12}$ (III.C.1).

IV. Synthesis of Urea

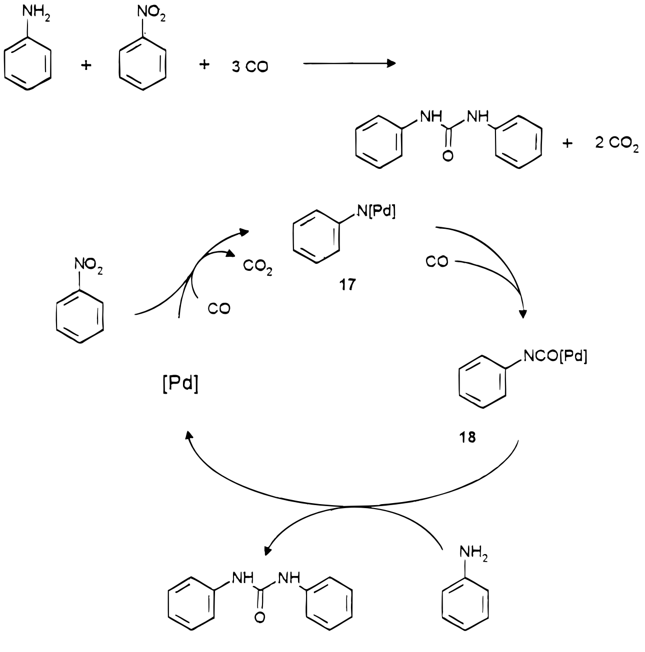
IV.A. Introductory Remarks

Phenyl ureas are a known class of commercially available herbicides. A typical method for the manufacture of ureas is the use of phosgene, which is toxic, expensive to handle, and generates lots of waste due to the workup of the chloride byproduct.[74] There is a continuing interest in comparatively mild conditions without using phosgene.[75] Several companies are pursuing routes, which are nonphosgenation processes, based on the reductive carbonylation of nitrobenzene to form *N*,*N*′-diphenylurea (DPU). The conventional N,N′-disubstituted urea is an important intermediate for the production of carbamates, which are raw materials for agrochemicals. The conventional method for preparing ureas is the reaction of amines with carbon monoxide in the presence of nonmetal catalysts such as *tert*-amine.[76] The yield of urea is increased only if excess sulfur is used for the reaction with amine. The use of sulfur produces hydrogen sulfide as an undesired byproduct, which raises the cost of the process because of its toxicity and its special handling in disposal. The other method utilizes selenium, which is a well-known toxic catalyst and which has to be precipitated by a continuous flow of oxygen.[77] Therefore industry has always been on the look out for new catalyst systems to make symmetric ureas and the more challenging unsymmetric ureas.

IV.B. Mechanism of the Formation of Symmetric Ureas

Two pathways can be envisioned on the catalytic formation of diphenylurea,[78] although they were not proven. The first pathway involves stoichiometric amounts of nitrobenzene and aniline, which form equimolar amounts of diphenylurea (Scheme 4). The palladium complex in this catalytic reaction does not undergo a redox cycle. It maintains the oxidation state throughout the catalytic cycle. The nitrobenzene is deoxygenated stepwise to form the nitrene complex **17**, which in turn reacts with CO to form phenyl isocyanate complex **18**. Complex **18** reacts with aniline to give the desired *N*,*N*′-diphenylurea. The catalytic cycle requires equimolar amounts of nitrobenzene and aniline.

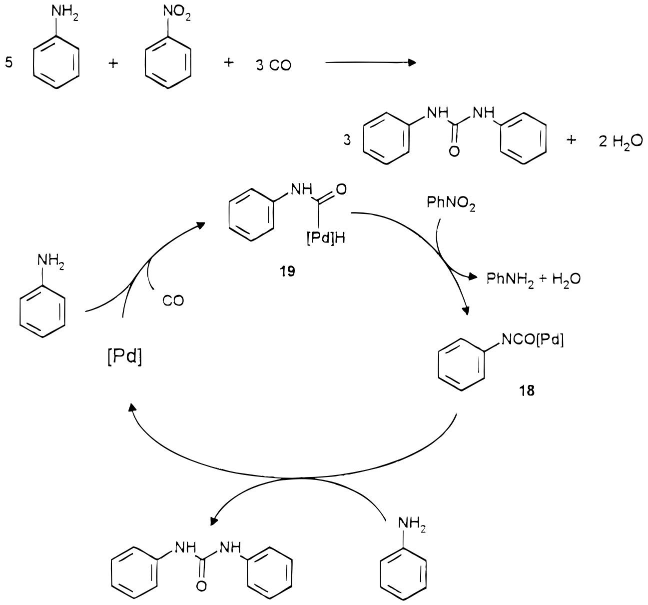
Scheme 4



The second pathway proceeds with a different stoichiometry, especially when excess aniline is used. The consumption of more aniline cannot be due to a reaction of aniline molecules with themselves, since no reaction is apparent without the use of nitrobenzene.

Since the reaction works well with 1 mol of nitrobenzene and 5 mol of aniline, a possible mechanism for such reaction is depicted in Scheme 5.[79]

Scheme 5



Aniline reacts with CO to give carbamoyl complex **19**. Aniline reacts further with complex **19** in the presence of nitrobenzene to give phenyl isocyanate complex **18**, which forms urea in analogy to the first pathway. Nitrobenzene in this case acts as an oxidizing agent by removing hydrogen from carbamoyl complex **19**. The net equation for the transformation of nitrobenzene to diphenyl urea is 5 mol of aniline for every mole of nitrobenzene.

The choice of either pathway depends on whether nitrobenzene or aniline is coordinated to the metal. If the nitrobenzene is first coordinated to the metal, a nitrene intermediate is formed by the deoxygenation. Insertion of CO into the nitrene complex produces a phenyl isocyanate complex, PhNCO[Pd], which reacts with aniline to form diphenyl urea according to the stoichiometry of Scheme 4.

IV.C. Synthesis of Symmetric Ureas

A method of high conversion and high yield of diarylurea involves the use of an excess of aniline as reagent and as solvent. Using xylene as solvent, excess aniline, nitrobenzene, palladium acetate, triphenylphosphine, and tetraethylammonium chloride as cocatalyst, the desired *N*,*N*′-diarylurea was obtained in 97% yield (Figure 9).[80]

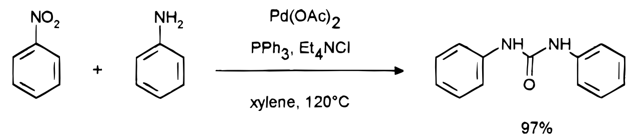


Figure 9.

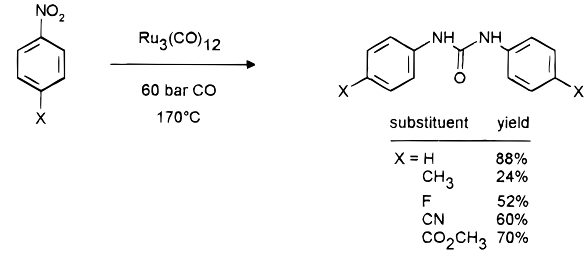


Figure 10.

When substituted nitro aromatic compounds were subjected to CO reduction in the presence of $Ru_3(CO)_{12}$ using *cis*-cyclooctene as solvent, symmetrical ureas were produced in variable yields depending on the substituents (Figure 10). Diphenylurea was obtained in 88% yield, whereas in the case of *p*-methyl substitution, yield decreased dramatically to 24%. Fluoro, cyano, and methoxycarbonyl groups in the para position led to the formation of the corresponding symmetric urea in 52%, 60%, and 70% yield, respectively.[81]

IV.D. Effect of Ligands, Cocatalysts, and Palladium Salts

A strong effect in the formation of ureas was observed when using different neutral ligands and palladium acetate as catalyst.[82] Several phosphorus monodentate ligands were tested (Table 6). The reaction proceeded rapidly using $P(n\text{-}Bu)_3$ and PPh_3 but slowly with $P(OEt)_3$ and $P(OPh)_3$. The initial reaction rate for various phosphorus compounds decreases in the following order: $P(n\text{-}Bu)_3 > PPh_3 \gg P(OEt)_3 > P(OPh)_3$, which is in accord with electron-donating ability of these ligands.[82a] In the bidentate case, phosphines of the general formula $Ph_2P(CH_2)_nPPh_2$ ($n = 1-6$) were used as ligands, and a great difference in the activity was observed when different chain lengths were investigated.[82b] The rate was negligible for $n = 1$, slightly greater for $n = 2$, and increased greatly for $n = 3$. After reaching a maximum for $n = 4$, the rate decreased again. It seems that the steric properties of the ligand play an important role in the catalytic activity. The proposed reaction pathways (section IV.B) involve a series of CO insertions, attacks by reactant, and substitutions at square planar palladium(II) complexes. It is commonly believed that such transformations proceed via a trigonal–bipyrimidal transition state. Therefore, bidentate ligands which are able to stabilize both the square planar ground state and the trigonal–bipyramidal transition state ($n = 2-5$) can catalyze the reaction effectively.

Table 6. Rate of Nitrobenzene Conversion to *N,N′*-Diphenylurea (DPU)[62]

ligands	% conversion	initial rate
$P(OPh)_3$	19	23
$P(OEt)_3$	24	32
PPh_3	100	89
$P(n\text{-}Bu)_3$	97	93
dppm ($n = 1$)		20
dppe ($n = 2$)		50
dppp ($n = 3$)		250
dppb ($n = 4$)		310
dppp ($n = 5$)		270
dpph ($n = 6$)		230
phen	100	93
TMphen	100	161

Table 7. Effect of Different Cocatalysts on the Formation of *N,N′*-Diphenylurea[83]

Pd salt	cocatalyst	% urea yield
$Pd(OAc)_2$	NEt_4Cl	98
$Pd(CF_3COO)_2$	NEt_4Cl	94
$PdCl_2$	NEt_4Cl	87
$Pd(OAc)_2$	KCl	49
$Pd(acac)_2$	NEt_4Cl	NR
Pd (metal)	NEt_4Cl	NR

It was found that both the electronic and steric effects of a ligand have a profound influence on the DPU formation from nitrobenzene, aniline, and CO. The characteristics of the ligand effects can be summarized as follows: (1) the greater the electron density on the palladium center, the higher the reaction rate, (2) the structure of bidentate ligands has a great effect on catalytic activity of DPU synthesis, and (3) bidentate ligands show a different reactivity from that of monodentate ligands.

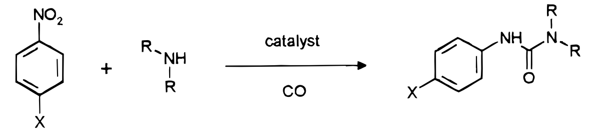
Palladium salts had a major effect on the course of reaction. When $Pd(OAc)_2$ and $PdCl_2$ were used under identical conditions, it was found that the nitrobenzene conversion was 98% and 87%, respectively. In contrast to this, $Pd(acac)_2$ or Pd metal did not show any activity under identical conditions. One might explain the lack of activity by the poor solubility of the palladium metal and the palladium salt. The use of a cocatalyst was important in these reactions. When tetraethylammonium chloride was used, the yield was high (>90%), but when the cocatalyst was changed to KCl, the yield dropped to 49%, and when $CuCl_2$ was used, no reaction took place[83] (Table 7).

V.E. Synthesis of Mixed Ureas

Phenyl ureas are a known class of commercially available herbicides. When 4-chloronitrobenzene was reacted with excess dimethylamine using palladium acetate, copper tosylate, and bipyridyl as catalyst system, it provided the desired product, *N,N*-dimethyl-*N′*-(4-chlorobenzene)urea, in 73% yield (Table 8, entry 1). It has been found that the yield of phenylureas can be increased by supplying amine continuously or stepwise during the period of reaction.[75] This might be explained by the fact that, in presence of low amine concentrations, reaction pathway 1 (Scheme 4) is more likely than reaction pathway 2 (Scheme 5). In the latter case, when amine and nitro compounds are used together, it is not possible to generate unsymmetric ureas in a selective way, as was found by Watanabe and Heck.[84]

Ureas were also prepared using catalytic amounts of $Pd(OAc)_2$ and dppp as ligand in the presence of acetic acid as cocatalyst (entry 2). The reaction yielded the desired urea in 98% conversion and 57%

Table 8. Synthesis of Unsymmetric Ureas by Reductive Carbonylation Using Different Catalysts



entry	catalyst	T (°C)	p (bar)	X	R	% yield
1[75]	$Pd(OAc)_2$/bipy/$Cu(OTos)_2$	140	50	Cl	Me	73
2[85]	$Pd(OAc)_2$/dppp/HOAc	110	60	H	Et	57
3[85]	$Rh(acac)(CO)_2$/dppp/$Cu(OAc)_2$	110	60	H	Et	70

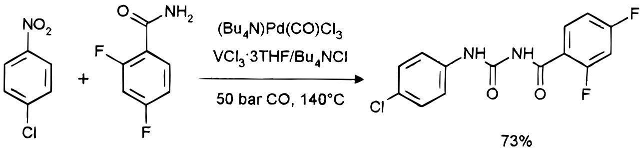


Figure 11.

selectivity. When using rhodium as catalyst, instead of palladium, and copper acetate as cocatalyst under the same reaction conditions mentioned above, the reaction produced the desired urea in 70% selectivity (80% conversion)[85] (entry 3). It is also possible to apply amides instead of amines as coreagents. With $(Bu_4N)Pd(CO)Cl_3$ as catalyst in the presence of VCl_3·THF, 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)-urea was prepared in 73% yield.[86a] Alternatively, $Pd(OAc)_2$/*p*-TosOH/bipy can be used as catalyst system in this reaction[86b] (Figure 11).

V. Synthesis of Amines

V.A. Introductory Remarks

Aromatic amines are important intermediates in the fine chemical, dye, and pigment industry.[87] Aromatic amines are produced by reduction of the corresponding nitro aromatics with a metallo hydride reagent or by catalytic hydrogenation.[88] The selective reduction of nitro aromatic groups in the presence of sensitive functional groups, e.g. carbonyl, cyano, chloro, and alkenic groups, with hydrogen is often difficult, because these sensitive functionalities are reduced faster with hydrogen than the nitro group.[89] Thus when 4-chloro-3-nitroacetophenone (**20**) is subjected to catalytic reduction, the chloro group is reduced (substituted by hydrogen), the nitro group is converted to an amino, and the carbonyl group is hydrogenated to a hydroxy (Figure 12).[90]

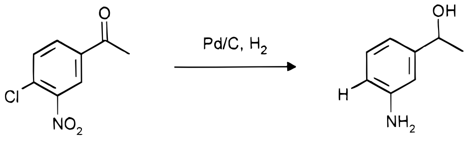


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Figure 12.

Also, palladium complexes of tertiary phosphines generated in situ from $Pd(OAc)_2$ with the corresponding phosphine ($L = i\text{-}Pr_3P$) and hydrogen were shown to reduce aromatic halides to dehalogenated aromatics.[91] The deoxygenation of nitro aromatics with CO as reducing agent in the presence of water was found to be an interesting alternative to the above mentioned methods.

V.B. Water–Gas Shift (WGSR) and Related Reactions

The WGSR has drawn considerable attention from the view point of carbon monoxide utilization in the chemical industry.[92] It represents very important industrial exploitation of CO in order to produce hydrogen.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The WGSR was pioneered by Reppe more than 40 years ago.[93] One application related to WGSR is the utilization of a metal complex under CO/H_2O conditions in reactions such as hydrogenation, hydroformylation, hydromethylation, and hydrocarbonylation.[94]

Another application related to WGSR is the reduction of nitro aromatics under CO/H_2O conditions using homogeneous catalysis (Figure 13). The first complex examined was $Fe(CO)_5$, which is converted to the catalyticaly active species $HFe(CO)_4$ by nucleophilic attack of OH^-.[95] Subsequently, many catalyst systems have been developed based on transition metal carbonyl complexes. Alper found that the reaction proceeds under atmospheric CO pressure at room temperature using $Ru_3(CO)_{12}$ in a benzene/2-methoxyethanol/5 N NaOH solution in the presence of a phase transfer catalyst.[96] Kaneda reported that amine and diamine-added $Rh_6(CO)_{16}$ in a 2-ethoxyethanol/H_2O solution showed catalytic activities for the reduction of nitrobenzene,[97] and Alessio found that $Rh_6(CO)_{16}$/phenanthroline catalyst was active in this reaction.[98] Other examples are $PhCCo_3(CO)_9$[99] and $Pt(PPh_3)_2Cl_2/Et_3N/SnCl_4$.[100]

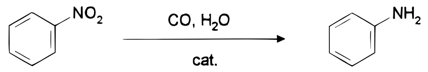


Figure 13.

Recently Nomura extensively investigated rhodium and ruthenium carbonyl clusters in the presence of amine or phosphine ligands.

The reduction of nitrobenzene using $Rh_4(CO)_{12}$ as catalyst at atmospheric CO pressure and room temperature was carried out in the presence of 2-methoxyethanol/5 N NaOH. The addition of an aqueous NaOH solution was very important for this reaction to proceed at a remarkable rate.[101] The rate also markedly increased with the addition of chelate phosphine ligands such as dppm, dppe, dppp, whereas it decreased with the addition of PPh_3.[102] A similar effect was observed when using $Ru_3(CO)_{12}$ and $Rh(CO)_2$acac complexes. The influence of the electronic and steric properties of phosphine ligands was investigated with $Rh(CO)_2(acac)$ as catalyst (Table 9).[101] When the ligand exhibits electrophilic character, it appears to help activate the water as previously pointed out for WGSR using a phosphine-coordinated rhodium carbonyl complex.[103] However, with electron-donating and bulky phosphine ligands such as $P(i\text{-}Pr)_3$, $P(t\text{-}Bu)_3$, and $P(Cy)_3$, activities were low, suggesting the importance of both electronic and steric factors for such reaction.

Table 9. Ligand Effect on the Reduction of Nitrobenzene to Aniline[101]

phosphine	OPR_3 (ppm)	cone angle	turnovers (mol/mol$_{cat}$)
none			5
PPh_3	−27	145	7
$PEtPh_2$	−33	140	14
PEt_2Ph	−42	136	116
PEt_3	−48	132	241
PCy_3	−50	170	35
$P(i\text{-}Pr)_3$	−55	160	27
$P(OEt)_3$	1	109	21
$P(OPh)_3$	18	128	39

Table 10. Effect of Reaction Temperature and CO Pressure on the Reduction of Nitrobenzene by a $Ru_3(CO)_{12}/Et_3N$ Catalyst[105]

entry	*T* (°C)	CO pressure (atm)	turnovers [mol$_{cat}^{-1}$]
1	150	20	1.582
2	180	20	2.058
3	180	50	10.500

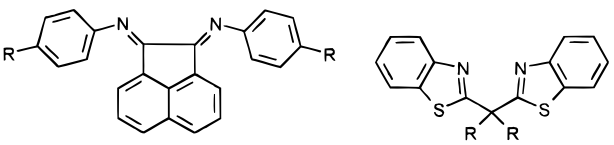
The phosphine ligand should be used in a 1:1 ratio with respect to the metal, because further added ligand is thought to suppress coordination of the nitro group to the metal center.

Temperature was shown to have a very important effect on the reaction rate. The turnovers of a $Rh(CO)_2(acac)/PEt_2Ph$ catalyst could be enhanced from 116 to 609 mol/mol per h by increasing the temperature from 25 to 50 °C. These results indicate that much greater catalytic activities may be achieved by using this catalyst system at higher reaction temperatures.[101]

Instead of phosphine ligands, amines can also be used. In analogy to the phosphines, an aqueous NaOH solution is necessary to obtain good results. The reaction rate increased upon addition of even small amounts of amine (amine/metal = 1.5:1), when using $Rh(CO)_2(acac)$, $Rh_4(CO)_{12}$, or $Rh_6(CO)_{16}$ as catalyst. It has to be noted that for each nitro compound the catalyst system consisting of $Rh(CO)_2(acac)$, $Rh_4(CO)_{12}$, or $Rh_6(CO)_{16}$ and an amine has to be optimized. Whereas 9,10-diaminophenanthrene is the most active amine in nitrobenzene reduction using $Rh(CO)_2acac$ as catalyst, NEt_3 is the most active one in the reduction of 1-nitroanthracene using $Rh_4(CO)_{12}$ as a catalyst, and 1,8-bis(dimethylamino)naphthalene was found to be the most active one in *p*-nitroanisole reduction in the presence of $Rh_6(CO)_{16}$.[104] It has to be noted that the attempts of Cenini to reproduce these catalytic systems have given negative results, which were explained by different kinds of stirring and heating apparatus. Also $Ru_3(CO)_{12}$ in the presence of amines such as Et_3N or $HN(iPr)_2$ (amine/metal = 70) exhibited significant catalytic activity. It was found that this system is very sensitive to temperature and to CO pressure, as can be seen in Table 10. When the temperature is increased from 150 to 180 °C and CO pressure from 20 to 50 bar, the turnovers of the catalyst are enhanced from 1582 to 10 500 mol/mol per h.[105]

Recently unique ligands such as **21** and **22** (Figure 14) have been reported by Cenini[106,107] for the reduction of nitrobenzene at 30 bar of CO and 165 °C.

The reaction is very sensitive to the substituent R in compound **21**, the order of activity being Me > Cl > OMe. Apparently the σ-donor ability of the substituent increases the activity, but a π-donor lowers it.



R = Me, Cl, OMe
21

R = Me, H
22

Figure 14.

The dimethylated derivative of **22** (R = Me) gave much better conversions (98%) and selectivities (75%) with respect to the nonmethylated one (R = H) (32%, 25%). It is assumed that in the case of R = H the ligand can be deprotonated when it is coordinating to the metal, thus affording a less active species.

V.C. Mechanism of the Deoxygenation Reaction

For most of the above mentioned catalyst systems the following was found: (a) when hydrogen was applied instead of CO, only trace amounts of product were formed, (b) CO was effectively consumed without accompanying hydrogen, and (c) reducible compounds such as benzonitrile, acetophenone, or styrene did not react.[105c] This strongly indicates that the reaction does not proceed by the hydrogenation of aromatic nitro compounds with hydrogen gas generated from the WGSR, although it is often mentioned in its context.

Therefore, it is presumed that the amine is formed by the deoxygenation of the nitro group to the corresponding nitrene species. The nitrene can either be converted to an amine by abstracting a proton from water or it can react with CO to give isocyanates, which react further with water to give phenylcarbamic acid, followed by hydrolysis to the desired amine (Figure 15).[108]

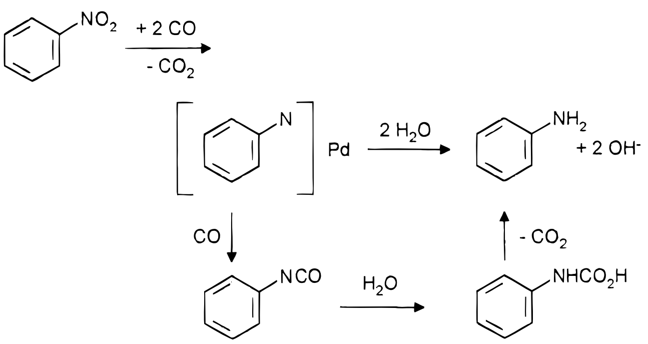


Figure 15.

It is also postulated that the reaction of aromatic nitro compounds involves successive oxygen transfer reactions between the nitro compounds and coordinated metal carbonyl ligand.[109]

In the case of the ruthenium catalyst $Ru_3(CO)_{12}$, it is assumed that the metal−carbonyl ligand undergoes cycloaddition with $PhNO_2$ and PhNO, followed by subsequent extrusion of carbon dioxide. The metal carbonyl reacts with CO/H_2O to give the aromatic amine (Figure 16).

Since the reaction with $Ru_3(CO)_{12}$ does not generate any hydrogen gas, it was postulated by the author that two possible reaction pathways can take place.

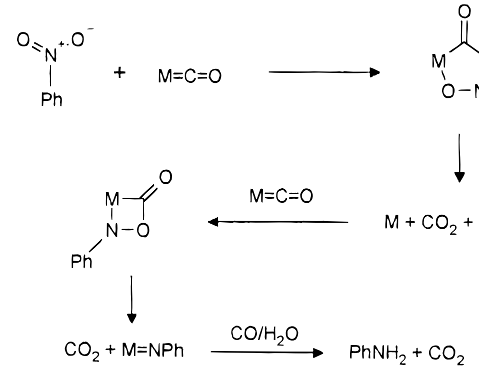


Figure 16.

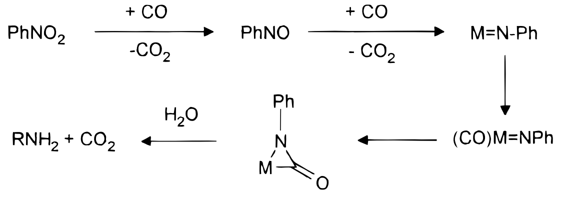


Figure 17.

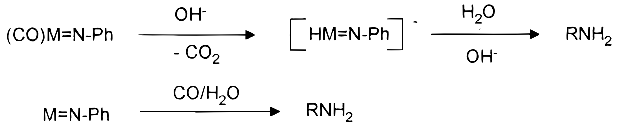


Figure 18.

The first pathway involves insertion of a metal to give the phenylnitroso intermediate followed by decarboxylation of the metal carbonyl with water[105c] (Figure 17) The second pathway involves the intramolecular hydrogen transfer between the metal nitrene and hydride (Figure 18).

V.D. Reduction of Nitro Aromatics Using CO in a Two-Phase System

The two-phase system using water soluble ligands such as TPPTS (**27**) and BINAS (**26**) for the reductive carbonylation of nitro aromatics is unique,[110] although two-phase systems have already been used in this reaction by Mestroni[98] and Alper.[96] It was possible to develop conditions where the nitro group can be selectively reduced to an amino in good yield.[110] Furthermore, this methodology ensures good product separation, due to the high solubility of the catalyst in water, whereas the product remains in the organic phase (Figure 19). Despite the advantages of using CO for the functionalization of nitro aromatics, the large amount of catalyst necessary and no efficient catalyst recycling have prevented the widespread use of such methodology. Two-phase catalysis with water soluble catalysts offers the most elegant principle for catalyst recycling in homogeneous catalysis.[111,112] As ligand, trisulfonated triphenylphosphine (TPPTS, **27**) and also a mixture of tetra-, penta-, and hexasulfonated binaphthyl called BINAS (**26**) (Figure 19)[113] were used.

As a model of the reaction, the reduction of **23** to **24** was studied. Interestingly, a ligand effect was found on the yield of the reaction. When the TPPTS/palladium ratio of 3, 5, or 10 was used, the reaction produced **24** in 40, 70, and 30% yield, respectively.

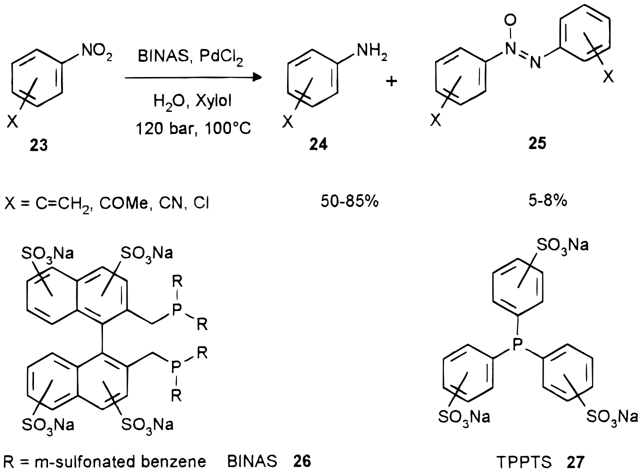


Figure 19.

When BINAS/palladium ratio of 1, 3, or 5 was used, the reaction produced **24** in 30, 85, and 50% yield, respectively. Upon dropping the temperature from 100 to 50 °C and the pressure from 120 to 60 bar, the yield of **24** decreased from 85% to 45% yield. The reaction also produced azoxy compound **25** as a byproduct, which was formed in significant amounts, if the temperature and pressure were lowered. Thus when the temperature was lowered from 100 to 50 °C and the pressure from 120 to 60 bar, **25** was formed in 15%.

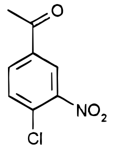
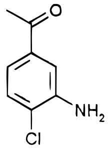
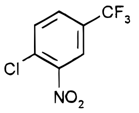
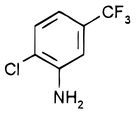
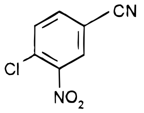
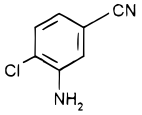
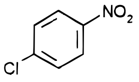
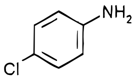
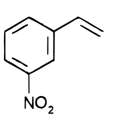
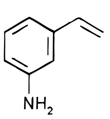
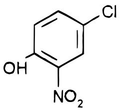
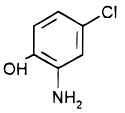
V.E. Selectivity in the Reduction of Nitro Aromatics

The use of water soluble ligands offers a new way to selectively reduce substituted aromatic nitro groups to amino groups in good yield in the presence of other sensitive functional groups, e.g., carbonyl, cyano, chloro, and alkenyl (Table 11). It was found that a nitro group can be reduced to the amino in the presence of chloro substituents (entries 1−4). Also, carbonyl and cyano groups, which are normally reduced to hydroxy and amino groups in the presence of hydrogen, are preserved by this methodology (entries 1 and 3). This method was also found to be selective with nitrostyrene, giving 3-aminostyrene in 50% isolated yield (entry 5). In most of the runs which were conducted using biphasic reduction conditions, it was found that BINAS is a better ligand than TPPTS for the reduction of nitro compounds to amines. This probably can be explained on the basis of substituents on phosphorus. BINAS contains methylene groups on the phosphorus, thus making the ligand more basic and the bidentate complex of BINAS/palladium more active toward CO reduction.

If an electron-donating group is present in the molecule, e.g., an OH group, the reduction is somewhat disappointing. The reduction of 2-nitro-4-chlorophenol using TPPTS or BINAS produced 2-hydroxy-5-chloroaniline in only 5% and 10% yields, respectively. Ru and Rh carbonyl clusters used as homogeneous catalysts also tolerate many functional groups that are very sensitive to reducing agents.[104,105,114]

The $Rh_6(CO)_{16}$/TMPDA catalyst system exhibited a highly chemoselective reduction of aromatic nitro group to the aromatic amino even in the presence of

Table 11. CO Reduction of Substituted Nitro Aromatic Compounds[a] [110]

entry	nitro compound	ligand	yield	aniline
1		TPPTS BINAS	65% 70%[b]	
2		TPPTS BINAS	45% 85%	
3		TPPTS BINAS	60% 60%	
4		TPPTS BINAS	40% 50%	
5		TPPTS	50%[b]	
6		TPPTS BINAS	5% 10%	

[a] Instrumental analysis data and ^{1}H-NMR, ^{13}C-NMR, IR, and MS spectra were fully consistent with the assigned structure. [b] Yield refers to an isolated, pure material.

various substituted double bonds. It is also possible to use aminated polystyrene in place of TMPDA, which leads to an easy isolation of amino products from the reaction mixture by forming a polymer-bound Rh_6–carbonyl cluster. Thus the reduction of ethyl-2-nitrocinnamate afforded 97% of the desired ethyl-2-aminocinnamate with the homogeneous system and 92% using the heterogeneous system (Figure 20). Poor reactivity of the Rh catalyst system has been observed in the chemoselective reduction of α,β-unsaturated aldehydes, whereas nitrostyrene derivatives, nitrocinnamates, and their diene derivatives as well as bromonitrobenzene were converted with yields in the range of 85–97%.[114]

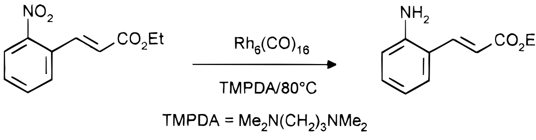


Figure 20.

When $Ru_3(CO)_{12}$ was used as a catalyst in the presence of an amine, the reaction produced desired product in 99% yield. The reduction proceeded with high selectivity in the nitro group reduction. The amine did not have an effect on the selectivity. Thus HN(i-Pr)$_2$, NEt_3, or piperidine could be used. Other functional groups were resistant to such reduction, e.g., cyano, carbonyl, and chloro groups (Figure 21).[105]

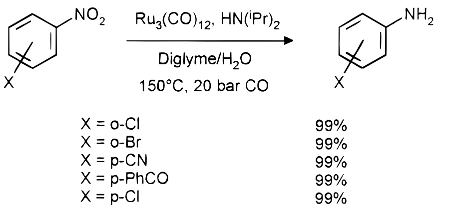


Figure 21.

VI. Intramolecular Cyclization Reactions

In this section a short overview of the most important intramolecular cyclization reactions is given.

When reacting an aromatic nitro compound with a hydroxyalkyl group in the ortho position in the presence of a Pd(TMB)$_2$/TMphen/TMBA or a $Ru_3(CO)_{12}/NEt_4Cl$ catalyst, cyclic carbamates were obtained in high yields.[115] The palladium catalyst has been shown to be far superior to the ruthenium catalyst in this reaction as far as selectivity is concerned and can be used under much milder reaction conditions. The Ru catalyst only works properly using o-dichlorobenzene as solvent due to the solubility of the alkylammonium salt. For n = 2 the yield of the seven-membered cyclic carbamate decreases to 60% because of the formation of a dimeric product.

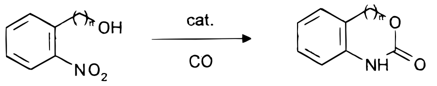
Since nitrene species are assumed to be intermediates in the deoxygenation of aromatic nitro compounds, these intermediates can be trapped by C=C, C=N, N=N, and C=O double bonds, yielding indoles, carbazoles, indazoles, benzimidazoles, triazoles, and quinazolinone.

Indoles can be prepared by deoxygenation of *o*-nitrostyrenes in an aprotic solvent using $PdCl_2(PPh_3)_2/SnCl_2$,[116] $M_x(CO)_y$ (M = Fe, Ru, Rh),[117,118] or Pd(TMB)$_2$/TMphen[119] as catalyst.

The reduction of the nitro moiety to aniline was observed as a side reaction. In the case of $M_x(CO)_y$ catalyst, quite harsh conditions were required (220 °C, 80 bar), whereas the Pd catalysts $PdCl_2(PPh_3)_2$ and Pd(TMB)$_2$/TMphen catalyze the reaction under considerably milder reaction conditions. Good yields of the corresponding indoles were observed in the case of R = Ph, COPh, C_4H_3S, or C_5H_4N.

It is also possible to trap the nitrene species by a double bond, which is part of an aromatic ring yielding carbazoles.[120,121] If a $Ru_3(CO)_{12}$ catalyst is used without a metal halide as cocatalyst, only small amounts of the desired product are observed, whereas aniline became the main product. It is assumed that the known chemical inertness of aromatic C–H bonds

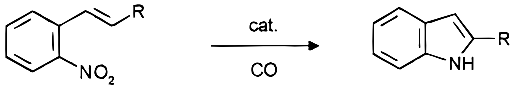
Table 12. Formation of Cyclic Carbamates[115]



catalyst[a]	n	p (bar)	T (°C)	% conversion	% selectivity
$Ru_3(CO)_{12}/Et_4NCl$[b]	1	60	170	99	51
Pd(TMB)$_2$/TMphen/TMBA[c]	1	40	140	100	99
Pd(TMB)$_2$/TMphen/TMBA[c]	2	40	140	100	60

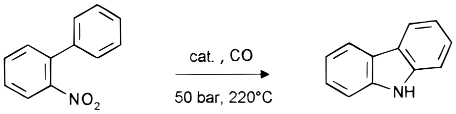
[a] Nitro compound/catalyst = 100. [b] Solvent, *o*-dichlorobenzene. [c] Solvent, toluene.

Table 13. Formation of Indoles



catalyst	nitro compound/catalyst	*T* (°C)	*p* (bar)	R	% conversion	% selectivity
$Fe(CO)_5$[117]	10	220	80	CO_2Me	100	75
$Ru_3(CO)_{12}$[117]	25	220	80	CO_2Me	100	33
$Rh_6(CO)_{16}$[117]	50	220	80	CO_2Me	100	59
$Pd(TMB)_2$/TMphen[119]	20	140	40	CO_2Me	100	75
$Pd(TMB)_2$/TMphen[119]	20	140	40	C_5H_4N	100	97
$Pd(TMB)_2$/TMphen[119]	20	140	40	Ph	99	85
$Pd(TMB)_2$/TMphen[119]	20	180	60	COPh	100	76
$Pd(TMB)_2$/TMphen[119]	20	100	20	COPh	100	52
$Pd(TMB)_2$/TMphen[119]	20	140	40	C_4H_3S	100	83
$PdCl_2(PPh_3)_2/SnCl_2$[116]	20	100	20	Ph	100	75
$PdCl_2(PPh_3)_2/SnCl_2$[116]	20	100	20	COPh	100	52

Table 14. Influence of Alkali Halides (MX) on the Product Distribution of Reductive Carbonylation of *o*-Nitrobiphenyl Catalyzed by $Ru_3(CO)_{12}$[121]



	% yield		
MX	carbazole	*o*-aminobiphenyl	5*H*-phenanthridin-6-one
	28	50	
NaF	43	11	37
NaCl	60	12	28
NaBr	46	13	40
NaI	12	15	52
LiCl	15	14	71

toward nitrene insertion and the stabilization of the intermediate aryl nitrene, which is coordinated in the ruthenium cluster $Ru_3(\mu_3\text{-}NC_6H_4\text{-}o\text{-}C_6H_5)_2(CO)_9$, are probably responsible for the poor yield of heterocyclic products. The presence of other species capable of coordinating the ruthenium atom with the consequent opening of at least one Ru−N bridge should increase the reactivity of the intermediate. In agreement with this assumption, catalytic amounts of sodium halides strongly affect the rate of reaction and product distribution (Table 14). Preference of carbazole is in order $Cl^- > Br^- \sim F^- > I^-$, whereas the selectivity for 5*H*-phenathridin-6-one is the reverse, $I^- > F^- \sim Br^- > Cl^-$. The formation of the aminobiphenyl is strongly decreased in the presence of halides. The role of cation was also investigated, showing that the exchange of Na against Li favors the formation of the 5*H*-phenathridin-6-one. This is explained by the higher polarizing capability of Li toward CO, promoting its insertion through an isocyanate intermediate.

Also other C═C double bond systems such as 2-nitrochalcones were applied in this intramolecular cyclization reaction using compound **21** (R = Me) as ligand. 2-Substituted-4-quinolones and 2,3-dihydro-2-substituted-4-quinolones were generated[122] as products.

Beside C═C double bonds, C═N double bonds can be applied in this cyclization reaction. Both *N*-(2-nitrobenzyliden)amine and 2-nitro-*N*-(phenylmethylene)benzeneamine can be used having the nitrogen atom at different positions. For the production of 2-phenylbenzimidazole, $Ru_3(CO)_{12}$[123,124] and $Pd(TMB)_2$/TMphen/TMBA[119] can be used as the catalyst system (Figure 22 and Table 15). Since the number of stable 2-nitro-N-(phenylmethylene)benzeneamine derivatives is rather limited, the imine is often generated in situ from 2-nitroaniline and aldehyde. On the other hand, this procedure causes the generation of 2(1*H*)-benzimidazolone as side product, derived by direct carbonylation of *o*-nitroaniline. Another side reaction is the deoxygenation of the nitro group, giving aniline derivatives. The distribution of the products depends on the catalyst system used and the reaction conditions. It is possible to use a broad varity of aldehydes when using $Ru_3(CO)_{12}$ as catalyst, whereas $Pd(TMB)_2$/TMphen/TMBA is limited to a small number.

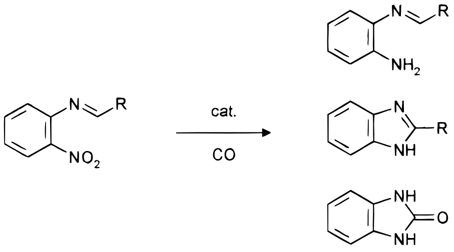


Figure 22.

Table 15. Formation of 2-Phenylbenzimidazoles by Reductive Carbonylation of 2-Nitro-*N*-(phenylmethylene)benzeneamine

catalyst	*T* (°C)	*p* (bar)	R	% conversion	% selectivity
$Ru_3(CO)_{12}$[a] [123,124]	220	50	*p*-Cl	100	82
$Ru_3(CO)_{12}$[b] [123,124]	220	50	*p*-Cl	100	73
$Pd(TMB)_2$/TMphen/ TMBA[c] [125]	180	40	*p*-Me	100	80

[a] Starting material, 2-nitro-*N*-(phenylmethylene)benzeneamine; starting material/catalyst = 43. [b] Starting material, 2-nitroaniline + benzaldehyde; starting material/catalyst = 43. [c] Starting material, 2-nitroaniline + benzaldehyde; starting material/catalyst = 20.

The generation of 2*H*-imidazole from *N*-(2-nitrobenzylidene)amine derivatives failed with $Ru_3(CO)_{12}$ as catalyst[123] but succeeded with $PdCl_2(PPh_3)_2/SnCl_2$ (Figure 23).[126] In the latter case the reaction proceeded smoothly at 20 bar and 100 °C, tolerating alkyl, aryl, methoxyalkyl, and chlorophenyl groups as R. The yields are in the range of 51−83%.

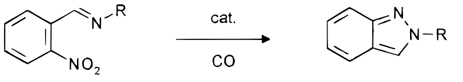


Figure 23.

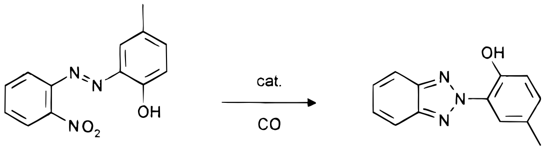


Figure 24.

The reductive carbonylation of *o*-nitrophenylazo compounds to yield the corresponding benzotriazoles in dichlorobenzene or *o*-xylene at 180–200 °C and 70–80 bar is catalyzed by $Ru_3(CO)_{12}$,[127] although with rather low conversion and selectivity. Both conversion and selectivity are markedly increased by addition of a base such as Et_3N (Figure 24).

It is assumed that Et_3N deoxygenates the nitro group under the present conditions to form $Et_3N\rightarrow O$, which in turn transfers the oxygen to CO with the formation of CO_2. Using *N*-(2-nitrobenzoyl)amides as substrates, it was possible to trap the intermediate nitrene species with a C═O double bond, yielding 4(3*H*)-quinazolinone derivatives. Several ruthenium and platinum complexes were found to be effective catalysts.[128]

VII. Conclusion

The use of CO in the reductive carbonylation of aromatic nitro compounds is very important not only from an academic point of view but also from an industrial one. Its versatility, low cost, and ease of accessability make it very attractive to the researcher. Its application should find use in the production of agricultural chemicals, pesticides, high-performance plastics, polyurethanes, elastomers, and adhesives, and its selective formation of functionalized products can find use in pharmaceuticals as well as the fine chemical industry. It was found that for each reaction and even for each substrate the catalyst system has to be optimized in view of metal complex, ligand, counterion, and cocatalyst. In most cases, best results were obtained only when large amounts of catalyst were used. Commercially, these reactions will only become of interest if the amount of catalyst is dramatically reduced. Therefore, in the future, it is very important to understand the mechanism of each reaction type and the reasons behind the deactivation of the catalyst. Only then can a catalyst system suitable for industrial application be found.

References

(1) Pisano, C.; Consiglio, G. *Gazz. Chim. Ital.* **1994**, *124*, 393.
(2) (a) Alper, H.; El Ali, B. *J. Mol. Catal.* **1993**, *80*, 377. (b) Alper, H.; Lee, C. W. *J. Org. Chem.* **1995**, *60*, 250.
(3) (a) Alper, H.; Grushin, V. *J. Am. Chem. Soc.* **1995**, *117*, 4305. (b) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. In *Carbonylation. Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (c) Alper, H.; Grushin, V. *Chem. Rev.* **1994**, *94*, 1047.
(4) Okano, T.; Harada, N.; Kiji *J. Bull. Chem. Soc. Jpn.* **1994**, *67*, 2329.
(5) Tori, S.; Okumoto, H.; Sadakane, M.; He Xu, L. *Chem. Lett.* **1991**, 1673.
(6) (a) Kushino, Y.; Itoh, K.; Miura, M.; Nomura, M. *J. Mol. Catal.* **1994**, *89*, 151. (b) Alper, H.; Jong-Tae, L. *Tetrahedron Lett.* **1991**, *32*, 1769. (c) Alper, H.; Satyanarayana, N. *Organometallics* **1991**, *10*, 804. (d) Tamaru, Y.; Hojo, M.; Yoshida, Z. Y. *J. Org. Chem.* **1991**, *56*, 1099. (e) Arzoumanian, H.; Cochini, F. *Organometallics* **1993**, *12*, 1871. (f) Hiyama, T.; Wakasa, N.; Ueda, T.; Kusumoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 640.
(7) (a) Alper, H.; Zargarian, D. *Organometallics* **1991**, *10*, 2914. (b) Yamamoto, A.; Ozawa, F.; Osakada, K.; Huang, L.; Son, T. I.; Kwasaki, N.; Doh, M. K. *Pure Appl. Chem.* **1991**, *63*, 687.
(8) Alper, H.; Eisenstat, A.; Satayanarayana, N. *J. Am. Chem. Soc.* **1990**, *112*, 7060.
(9) (a) Drent, E. EP 0399617, 1990; *Chem. Abstr. 114*, 165108. (b) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661. (c) Brookhart, M.; Rix, F. C.; Desimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894.
(10) (a) Erpenbach, H.; Gehrmann, K.; Kubbeler, K. H. EP 0008396, 1980; *Chem. Abstr. 93*, 45992*m*. (b) Forster, D.; Singleton, T. C. *J. Mol. Catal.* **1982**, *17*, 299.
(11) Armor, J. N. *App. Catal.* **1991**, *78*, 141.
(12) Cenini, S.; Pizzotti, M.; Crotti, C. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, 1988; Vol. 6, p 97.
(13) Cenini, S. In *Industrial Application of Homogeneous Catalysis and Related Topics*; 1984; p 135.
(14) Ikariya, T. *Catalysis* **1989**, *31*, 271.
(15) Giannocarro, P. *J. Organomet. Chem.* **1987**, *336*, 271.
(16) Hardy, W. B.; Bennett, R. P. *Tetrahedron Lett.* **1967**, *11*, 961.
(17) Selivanov, V. D.; Konstatinov, I. I. *Russ. J. Phys. Chem.* **1975**, *49*, 620.
(18) Drent, E.; van Leeuwen, P. W. N. M. EP 86281, 1983.
(19) Röper, M. *Industrial Applications of Homogeneous Catalysis*; D. Reidel: Dordrecht, 1988.
(20) Cenini, S.; Crotti, C. *Metal promoted selectivity in organic synthesis*; Kluwer Academic Publishers: The Netherlands, 1991.
(21) Leconte, P.; Metz, F.; Mortreux, A.; Osborn, J. A.; Paul, F.; Petit, F.; Pillot, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1616.
(22) (a) Elleuch, B.; Taarit, Y. B.; Basset, J. M.; Kervennal, J. *Angew. Chem., Int. Ed.* **1982**, *21*, 687. (b) Abakumov, G. A.; Knyazeva, I. L.; Vavilina, N. N.; Gorbunova, L. V.; Zhivtsova, S. V. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1984**, *6*, 1352. (c) Weigert, F. J. *J. Org. Chem.* **1973**, *38*, 1316. (d) Manov-Yuvenskii, V. I.; Nefedov, B. K. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1979**, *9*, 2139. (e) Tietz, H.; Unverferth, K.; Schwetlik, K. *Z. Chem.* **1980**, *20*, 295. (f) Tietz, H.; Unverferth, K.; Schwetlik, K. *Z. Chem.* **1977**, *17*, 368. (g) Tietz, H.; Unverferth, K.; Schwetlik, K. *Z. Chem.* **1978**, *18*, 98. (h) Unverferth, K.; Höntsch, R.; Schwetlik, K. *J. Prakt. Chem.* **1979**, *321*, 86. (i) Unverferth, K.; Höntsch, R.; Schwetlik, K. *J. Prakt. Chem.* **1979**, *321*, 928. (j) Braunstein, P.; Bender, R.; Kervennal, J. *Organometallics* **1982**, *1*, 1236. (k) Nefedov, B. K.; Manov-Yuvenskii, V. I.; Khoshdurdyev, Kh. O. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, *7*, 1555. (l) Manov-Yuvensii, V. I.; Lapidus, A. L.; Petrovskii, K. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, *9*, 1709. (m) Nefedov, B. K.; Manov-Yuvenskii, V. I.; Khoshdurdyev, Kh. O. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, *1*, 113. (n) Gupte, S. P.; Chaudhari, R. V. *J. Mol. Catal.* **1986**, *34*, 241.
(23) Cenini, S.; Ragaini, F.; Pizzotti, M.; Porta, F.; Mestroni, G.; Alessio, E. *J. Mol. Catal.* **1991**, *64*, 179.
(24) Nefedov, B. K.; Manov-Yuvenskii, V. I.; Gorbunova, L. V.; Vavilina, N. N.; Smetanin, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 205.
(25) Razuvaev, G. A.; Nefedov, B. K.; Manov-Yuvenskii, V. I.; Gorbunova, L. V.; Vavilina, N. N.; Chimishkyan, A. L.; Smetanin, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2567.
(26) Nefedov, B. K.; Manov-Yuvenskii, V. I. *Russ. Chem. Rev.* **1981**, *50*, 470.
(27) Drent, E. EP 334292, 1986.
(28) (a) Gupte, S. P.; Chaudhari, R. V. *J. Mol. Catal.* **1984**, *24*, 197. (b) Halligudi, S. B.; Chaudhari, R. V.; Doraiswamy, L. K. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 794.
(29) Ugo, R.; Psaro, R.; Pizzotti, M.; Nardi, P.; Dossi, C.; Andreetta, A.; Capparella, G. *J. Organomet. Chem.* **1991**, *417*, 211.
(30) Takagi, E.; Inoue, K.; Ikeda, K.; Tsumura, R. *Appl. Catal. A: General* **1994**, *119*, N20.
(31) (a) Watanabe, Y.; Tsuji, Y.; Takeuchi, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3011. (b) Watanabe, Y.; Tsuji, Y.; Takeuchi, R.; Suzuki, N. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3343. (c) Watanabe, Y.; Tsuji, Y.; Suzuki, N. *Chem. Lett.* **1982**, 105.
(32) Gorbunova, L. V.; Knyazeva, I. L.; Nefedov, B. K.; Khoshdurdyev, K. O.; Manov-Yuvenskii, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *7*, 1644.
(33) Alper, H.; Hashem, K. E. *J. Am. Chem. Soc.* **1981**, *103*, 6514.
(34) Shell, EP 86281, 1981.
(35) Grob, C. A.; Schiess, P. W. *Angew. Chem.* **1967**, 1.
(36) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1988**, *53*, 1243.
(37) Skoog, S. J.; Campbell, J. P.; Gladfelter, W. L. *Organometallics* **1994**, *13*, 4137.
(38) (a) Sherlock, S. J.; Boyd, D. C.; Moasser, B.; Gladfelter, W. L. *Inorg. Chem.* **1991**, *30*, 3626. (b) A referee commented that the proposed first step of the reaction is an electron transfer from

the metal to the organic nitro compound and it is now emerging as a more acceptable mechanism. This explains why only low oxidation state transition metal complexes can act as catalysts in this reaction.

(39) Gargulak, J. D.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1991**, *113*, 1054.
(40) (a) Gargulak, J. D.; Berry, A. J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 8933. (b) Gargulak, J. D.; Gladfelter, W. L. *Inorg. Chem.* **1994**, *33*, 253.
(41) Gargulak, J. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 3792.
(42) Ragaini, F.; Cenini, S.; Fumagalli, A.; Crotti, C. *J. Organomet. Chem.* **1992**, *428*, 401.
(43) Liu, C.; Chang, C. *J. Organomet. Chem.* **1992**, *420*, 119.
(44) Ragaini, F.; Cenini, S.; Demartin, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1467.
(45) Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1994**, *13*, 1178.
(46) Wehman, P.; Borst, L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. submitted to *Chem. Eur. J.*
(47) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1286.
(48) Cenini, S.; Pizzotti, M.; Crotti, C.; Ragaini, F.; Porta, F. *J. Mol. Cat.* **1988**, *49*, 59.
(49) (a) Grate, J. H.; Hamm, D. R.; Valentine, D. H. WO 85/01285, 1985. (b) Grate, J. H.; Hamm, D. R.; Valentine, D. H. WO 86/05179, 1986. (c) Grate, J. H.; Hamm, D. R.; Valentine, D. H. WO 86/05178, 1986. (d) Grate, J. H.; Hamm, D. R.; Valentine, D. H. US 4705883, 1987. (e) Grate, J. H.; Hamm, D. R.; Valentine, D. H. US 4629804, 1986. (f) Grate, J. H.; Hamm, D. R.; Valentine, D. H. US 4603216, 1986. (g) Grate, J. H.; Hamm, D. R. US 4709073, 1987. (h) Grate, J. H.; Hamm, D. R.; Valentine, D. H. US 4600793, 1986. (i) Grate, J. H.; Hamm, D. R.; Valentine, D. H. US 4687872, 1987.
(50) (a) Han, S.-H.; Geoffroy, G. L. *Polyhedron* **1988**, *7*, 2331. (b) Han, S.-H.; Song, J.-S.; Macklin, P. D.; Nguyen, S. T.; Geoffroy, G. L. *Organometallics* **1989**, *8*, 2127.
(51) (a) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S.; Shaikh, Z. A. *J. Mol. Catal.* **1990**, *57*, 301. (b) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S.; Shaikh, Z. A. *J. Mol. Catal.* **1990**, *57*, 307.
(52) Halligudi, S. B.; Bhatt, K. N.; Khan, N. H.; Taqui Khan, M. M. *J. Mol. Catal.* **1992**, *72*, 139.
(53) Mukherjee, D. K.; Palit, B. K.; Saha, C. R. *J. Mol. Catal.* **1994**, *91*, 19.
(54) (a) Alessio, E.; Mestroni, G. *J. Organomet. Chem.* **1985**, *291*, 117. (b) Tumanova, A. R.; Pirozhkov, S. D.; Lapidus, A. L. *Khim. Tverd. Topl.* **1992**, *3*, 55-9; *Chem. Abstr. 117*, 253854.
(55) Chaudari, B. M.; Sharma, G. V. M.; Bharathi, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 465.
(56) Valli, V. L. K.; Alper, H. *J. Am. Chem. Soc.* **1993**, *115*, 3778.
(57) Chaudari, B. M.; Koteswara, K.; Pirozhkov, S. D.; Lapidus, A. L. *J. Mol. Catal.* **1994**, *88*, 23.
(58) (a) Hirai, H.; Miyata, K.; Soga, M.; Hasegawa, S. JP 7924853, 1979; *Chem. Abstr. 90*, 203736a. (b) Becker, R.; Groling, J.; Rasp, C.; Scharfe, G. DE 2819826, 1980. (c) Lapidus, A. L.; Pirozhkov, S. D.; Tumanova, A. R.; Dolidze, A. V.; Yukhimenko, A. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, *8*, 1885. (d) Iwata, K.; Kurachi, K. *Sekiyu Gakkaishi* **1991**, *34*, 160; *Chem. Abstr. 114*, 209532.
(59) Alessio, E.; Mestroni, G. *J. Mol. Catal.* **1984**, *26*, 337.
(60) (a) Drent, E.; van Leeuwen, P. W. N. M. EP 86281, 1983. (b) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661.
(61) Bontempi, A.; Alessio, E.; Chanos, G.; Mestroni, G. *J. Mol. Catal.* **1987**, *42*, 67.
(62) (a) Zhang, F.; Wang, W.; Wang, J.; Xu, J.; Xu, P. *Xiamen Daxue Xuebao, Zi ran Kexueban* **1991**, *30*, 41; *Chem. Abstr. 116*, 138635. (b) Wang, J.; Xu, P.; Zhang, F. *Fenzi Cuihua* **1990**, *4*, 226; CA 114, 184934.
(63) Wehman, P.; Dol, G. C.; Moorman, E. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1994**, *13*, 4856.
(64) Wehman, P.; Kaasjager, V. E.; de Lange, W. G. J.; Hartl, F.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 3751.
(65) Wehman, P.; Borst, L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M., submitted to *J. Chem. Soc., Dalton Trans.*
(66) (a) Zhang, F.; Wang, W.; Xu, P.; Xu, J. *Fenzi Cuihua* **1991**, *5*, 372; *Chem. Abstr. 116*, 128307. (b) Zhang, F.; Wang, W.; Huang, W.; Long, R.; Xu, P.; Xu, J. *Xiamen Daxue Xuebao, Ziran Kexueban* **1993**, *32*, 177; *Chem. Abstr. 121*, 107754.
(67) Reddy, N. P.; Masdeu, A. M.; Ali, B. E.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 863−4.
(68) Wehman, P. *Thesis*, 1995, University of Amsterdam, chapter 4.
(69) Izumi, Y.; Satoh, Y.; Urabe, K. *Chem. Lett.* **1990**, 795.
(70) Izumi, Y.; Satoh, Y.; Kondoh, H.; Urabe, K. *J. Mol. Catal.* **1992**, *72*, 37.
(71) Lee, J. S.; Woo, J. W.; Lee, C. W.; Hong, K. S.; Yeo, J. K. *Korean J. Chem. Eng.* **1990**, *7*, 145.
(72) Wehman, P.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.*, in press.
(73) Rode, C. V.; Gupte, S. P.; Chaudhari, R. V.; Pirozhkov, C. D.; Lapidus, A. L. *J. Mol. Catal.* **1994**, *91*, 195.
(74) March, J. *Advanced Organic Chemistry*; John Wiley & Sons: New York, 1985; p 370.
(75) Goodall, B. L. EP 319 111, 1989.
(76) Franz, R. A.; Applegath, F.; Morriss, F. V.; Baiocchi, F. *J. Org. Chem.* **1961**, *26*, 3309.
(77) Sonoda, N.; Yasuhara, T.; Kondo, K.; Ikeda, T. *J. Am. Chem. Soc.* **1971**, *93*, 6344.
(78) (a) Lee, C. W.; Lee, S. M.; Oh, J. S. *Ind. Eng. Chem. Res.* **1991**, *30*, 1456. (b) Lee, S. M.; Cho, N. S.; Kim, K. D.; Oh, J. S.; Lee, C. W.; Lee, J. S. *J. Mol. Catal.* **1992**, *73*, 43.
(79) Kim, K. D.; Lee, S. M.; Cho, N. S. *J. Mol. Catal.* **1992**, *75*, L1−L6.
(80) Oh, J. S.; Lee, Sang, M. L. US 5198582, 1993.
(81) Ridone, B.; Bassoli, A.; Cenini, S. *J. Mol. Catal.* **1991**, *66*, 163.
(82) (a) Lee, C. W.; Lee, J. S. *J. Mol. Catal.* **1993**, *81*, 163. (b) Lee, C. W.; Lee, S. M.; Oh, J. S.; Lee, J. S. *Catal. Lett.* **1993**, *19*, 217.
(83) Lee, A. M.; Lee, C. W. *J. Mol. Catal.* **1990**, *61*, L-15-L18.
(84) (a) Tsuji, Y.; Takeuchi, R.; Watanabe, Y. *J. Organomet. Chem.* **1985**, *290*, 249. (b) Dieck, H.; Laine, R.; Heck, R. K. *J. Org. Chem.* **1975**, *40*, 2819.
(85) Drent, E. EP 0250037, 1987.
(86) (a) Goodall, B. L. EP 0 398404, 1990. (b) Drent, E.; Prillwitz, P. E. EP 225673, 1987.
(87) Mestroni, G.; Camus, A.; Zassinovich in *Aspects of Homogeneous Catalysis*, Ugo, R.; Reidel: Dordrecht 1981, Vol. 4, p 71.
(88) Feuer, B.; Vincent, A. *J. Org. Chem.* **1965**, *31*, 2880.
(89) Rylander, P. in *Catalytic Hydrogenation in Organic Synthesis*; Academic Press: New York, 1979; p 122.
(90) Tafesh, A., unpublished results.
(91) Huser, M.; Osborn, J. A. EP 352164, 1990.
(92) (a) Laine, R. M.; Crawford, E. J. *J. Mol. Catal.* **1988**, *44*, 357. (b) Ford, P.; Rokicki, A. *Adv. Orgmet. Chem.* **1988**, *28*, 139.
(93) Reppe, W. *Justus Liebigs Ann. Chem.* **1953**, *582*, 1.
(94) For reviews, see: (a) Escaffre, P.; Thorez, A.; Kalck, P. *J. Mol. Catal.* **1985**, *33*, 87. (b) Sugi, Y. *Catalyst* **1983**, *25*, 4164.
(95) (a) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3969. (b) Cann, K.; Cole, T.; Ramage, R.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6184. (c) Jothimony, K.; Vancheesan, S.; Kuriacose, J. *J. Mol. Catal.* **1989**, *52*, 297.
(96) Alper, H.; Amaratuga, S. *Tetrahedron Lett.* **1980**, *21*, 2603.
(97) (a) Kaneda, K.; Hiraki, M.; Imanaka, T.; Teranishi, S. *J. Mol. Catal.* **1981**, *12*, 385. (b) Kaneda, K.; Hiraki, M.; Imanaka, T.; Teranishi, S. *J. Mol. Catal.* **1981**, *12*, 385. (c) Kaneda, K.; Yasumura, M.; Imanaka, T.; Teranishi, S. *J. Chem. Soc., Chem. Commun.* **1982**, 935.
(98) Alessio, E.; Zassinovich, G.; Mestroni, G. *J. Mol. Catal.* **1983**, *18*, 113.
(99) Miura, M.; Shinohara, M.; Nomura, M. *J. Mol. Catal.* **1988**, *45*, 151.
(100) Watanabe, Y.; Tsuji, Y.; Ohsumi, T.; Takeuchi, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2867.
(101) Nomura, K.; Ishino, M.; Hazama, M. *J. Mol. Catal.* **1993**, *78*, 273.
(102) Nomura, K.; Ishino, M.; Hazama, M. *J. Mol. Catal.* **1991**, *65*, L5.
(103) Yoshida, T.; Thorn, D. L.; Okano, T. *J. Am. Chem. Soc.* **1980**, *102*, 4212.
(104) (a) Nomura, K.; Ishino, M.; Hazama, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2624. (b) Nomura, K.; Ishino, M.; Hazama, M. *J. Mol. Catal.* **1991**, *66*, L1.
(105) (a) Nomura, K. *J. Mol. Catal.* **1992**, *73*, L1. (b) Nomura, K. *Chem. Lett.* **1991**, 1679. (c) Nomura, K. *J. Mol. Catal. A: Chemical* **1995**, *95*, 203.
(106) Ragaini, F.; Cenini, S.; Tollari, St. *J. Mol. Catal.* **1993**, *85*, L1.
(107) Ragaini, F.; Pizzotti, M.; Cenini, S.; Abbotto, A.; Pagani, G.; Demartin, F. *J. Organomet. Chem.* **1995**, *489*, 107.
(108) (a) Rode, C. V.; Gupta, S. P.; Chaudhari, R. V.; Pirozhkov, C. D.; Lapidus, A. L. *J. Mol. Catal.* **1994**, *91*, 195. (b) Iqbal, A. F. M. *J. Org. Chem.* **1972**, *37*, 2791.
(109) (a) Sheldon, R. A. *Chemical from Synthesis Gas*; Reidel: Dordrecht, 1989; Vol. 5, p 271. (b) Ikariye, T. *Shokubai Catalyst* **1989**, *5*, 271.
(110) Tafesh, A.; Beller, M. *Tetrahedron Lett.* **1995**, *36*, 9305. Tafesh, A.; Beller, M.; Kohlpaintner, C.; Naumann, C. EP 96102416.3, 1996. Tafesh, A.; Regnat, D.; Kleiner, H.-J.; Naumann, C. EP 96102415.5, 1996. Tafesh, A.; Beller, M. *Tetrahedron Lett.* **1996**, submitted for publication.
(111) Herrmann, W.; Kohlpainter, C. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524.
(112) Cornils, B.; Wiebus, E. *Chemtech* **1995**, 33.
(113) Herrmann, W.; Albanese, G. P.; Manetsberger, R. B.; Lappe, P.; Bahrmann, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1524.
(114) Kaneda, K.; Kuwahara, H.; Imanaka, T. *J. Mol. Catal.* **1994**, *88*, L267.
(115) Cenini, S.; Console, S.; Crotti, C.; Tollare, S. *J. Organomet. Chem.* **1993**, *451*, 157.
(116) Akazome, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1994**, *59*, 3375.

(117) Crotti, C.; Cenini, S.; Rindone, B.; Tollari, S.; Demartin, F. *J. Chem. Soc.; Chem. Commun.* **1986**, 784.
(118) Crotti, C.; Cenini, S.; Todeschini, R.; Tollari, S. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2811.
(119) Tollari, S.; Cenini, S.; Crotti, C.; Gianella, E. *J. Mol. Catal.* **1994**, *87*, 203.
(120) Crotti, C.; Cenini, S.; Bassoli, A.; Rindone, B.; Demartin, F. *J. Mol. Catal.* **1991**, *70*, 175.
(121) Pizzotti, M.; Cenini, S.; Quici, S.; Tollari, S. *J. Chem. Soc., Perkin Trans. 2* **1994**, 913.
(122) Tollari, St.; Cenini, S.; Ragaini, F.; Cassar, L. *J. Chem. Soc., Chem. Commun.* **1994**, 1741.
(123) Crotti, C.; Cenini, S.; Ragaini, F.; Porta, F. *J. Mol. Catal.* **1992**, *72*, 283.
(124) Bassoli, A.; Cenini, S.; Farina, F.; Orlandi, M.; Rindone, B. *J. Mol. Catal* **1994**, *89*, 121.
(125) Akazome, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1994**, *59*, 3375.
(126) Pizzotti, M.; Cenini, S.; Rinaldo, P.; Costanzi, S. *J. Mol. Catal.* **1990**, *63*, 299.
(127) Akazome, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1993**, *58*, 310.

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