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Catalytic synthesis of isocyanates or carbamates from nitroaromatics using Group VIII transition metal catalysts

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Contents

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Abstract

In order to produce various isocyanates, catalyzed carbonylations of nitroaromatic compounds constitute a set of very appealing reactions for industry. These environmentally benign reactions present many advantages over the traditional phosgene route actually used for isocyanate production. Group VIII metal complexes constitute currently the most interesting catalysts for these transformations and this review focuses on the academic research conducted in this field. After a brief introduction, some general data about the ‘direct’ and ‘indirect’ carbonylation processes is given and the most active catalytic systems developed for both transformations are described. Then, the mechanistic data available for specific catalytic systems are presented and the reaction schemes of these reactions thoroughly analyzed. Finally, industrial perspectives regarding reductive carbonylation reactions are briefly discussed before concluding. A review with 390 references.

Keywords: Nitroaromatic compounds; Carbonylation; Catalytic systems

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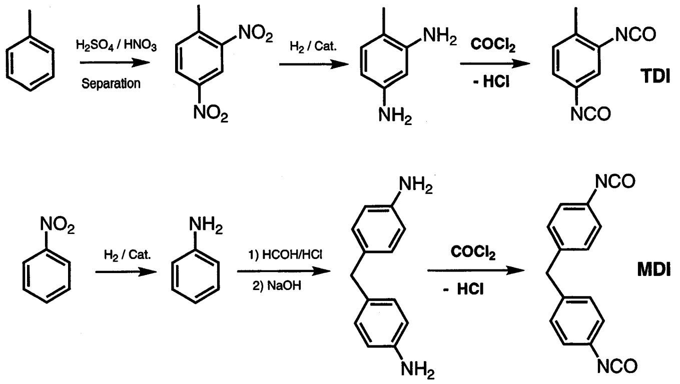
Nomenclature

Ar	aromatic
bipy	2,2′-bipyridine
^{n}Bu	*n*-butyl
^{t}Bu	*tert*-butyl
$(BOC)_2O$	di-*tert*-butyl carbonate
Cat.	catalyst
CB	chlorobenzene
p-CBA	*para*-chlorobenzoic acid
chel	chelating ligand
DBA	dibenzylideneacetone
dmphen	4,7-dimethyl-1,10-phenanthroline
DMAP	4-dimethylaminopyridine
DMC	dimethylcarbonate
DME	1,2-dimethoxyethane
DMP	1,2-dimethoxypropane
DMSO	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,2-bis(diphenylphosphino)propane
DPU	*N*,*N*′-diphenylurea
Et	ethyl
E_a	activation energy
HPA	heteropolyanion
isoquin	isoquinoline
L.A.	Lewis acid
[M] or M	metallic center
MDI	diphenylmethane diisocyanate
N–N	diimine
OAc	acetate
ODCB	*ortho*-dichlorobenzene
OMe	methoxy
OTMB	2,3,5,6-tetramethylbenzoate
OTf	triflate
Ph	phenyl
phen	1,10-phenanthroline
phpy	4-phenyl pyridine
PIC	phenyl isocyanate
Py	pyridine
PPN	μ-nitrido-bis(triphenylphosphonium)
r.d.s.	rate determining step
salen	bis(salicylaldehyde)-enamine
saloph	bis(salicylaldehyde)-*o*-phenylene diamine
tfa	trifluoroacetate
Ton	turnover number of a catalyst ((mol pdct/mol cat) h^{-1})

THF	tetrahydrofuran
TMBA	2,3,5,6-tetramethylbenzoic acid
tmphen	3,4,7,8-tetramethyl-1,10-phenanthroline
TrMBA	2,4,6-trimethylbenzoic acid
TPB	*N*,*N*′,*N*″-triphenyl-biuret
p-TSA	*para*-toluenesulfonic acid

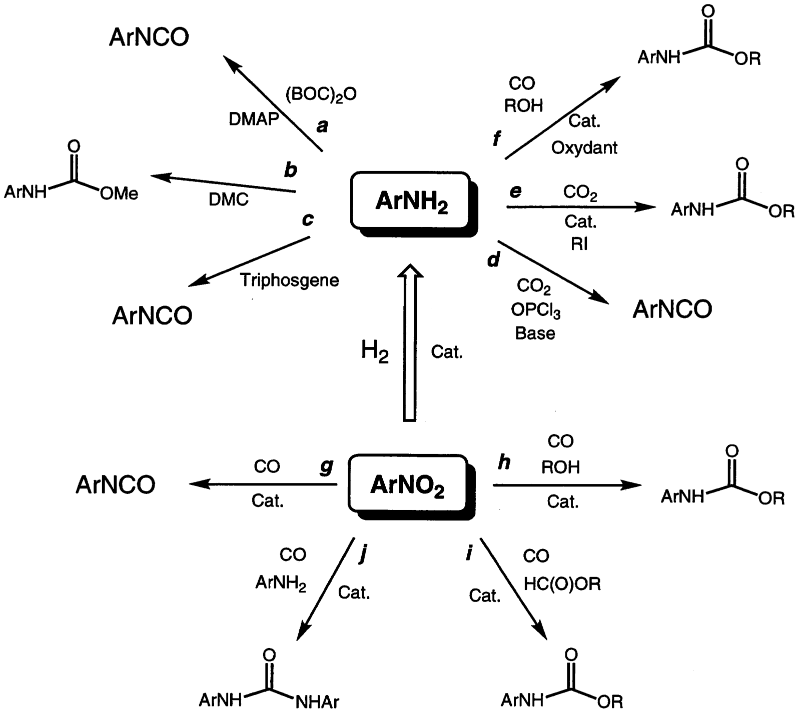
1. Introduction

Industrially, aromatic isocyanates represent very important intermediates [1]. In the polymer field for instance, polyisocyanates such as 2,4-toluene diisocyanate (TDI) or methylene 4,4′-diphenyl diisocyanide (MDI) are starting materials for the synthesis of many polyurethanes [2,3]. Moreover, aromatic isocyanates like phenyl isocyanate (PIC) or 3,4-dichlorophenyl isocyanate are key compounds in speciality chemicals as well, their carbamates derivatives intervene in the synthesis of various pesticides [4–9]. Aromatic isocyanates are currently synthesized by reduction and phosgenation from corresponding nitro compounds (see Scheme 1) [10]. This process has three major drawbacks: (i) first, the use of phosgene which is a very poisonous and flammable gas [11–13], therefore difficult to handle in bulk quantities; (ii) then, the formation of two equivalents molar amounts per nitro group of corrosive hydrochloric acid during the reaction which renders the medium very aggressive with time [14], and (iii) finally, the unavoidable inclusion of difficult-to-remove hydrolyzable chlorine containing compounds in the final product which can be detrimental for the further processing of the isocyanate [10,15].



Scheme 1.

During the last decades, starting from the aromatic amine, many other procedures to generate isocyanates (***a***, ***c***, ***d***) or carbamates (***b***, ***e***, ***f***) to limit these drawbacks have been developed (see Scheme 2) [16]. Some consist simply in replacement of phosgene by less dangerous carbonylating agents like carbonates (***a***) [17], (***b***) [18–21] or triphosgene (***c***) [22,23]. However, except perhaps for reaction (***b***) [21], the cost and availability of the phosgene substitute in these reactions is detrimental to the scaling up of these processes. Other approaches imply new catalytic reactions as carboxylation or carboalkoxylation to form, respectively, isocyanates (***d***) [24] and carbamates (***e***) [11,25–31] or oxidative carbonylation (***f***) yielding carbamates [15,32–35]. Notably, the latter process (***f***) was widely investigated with various catalysts [36–54]. More recently, electrochemical processes based on reaction (***e***) were proposed as well [55]. To our knowledge, except for the oxidative carbonylation reaction (***f***), all routes are still laboratory procedures (see Section 5.1).



Scheme 2.

A much more appealing synthetic alternative for industry to produce aromatic isocyanates would be to use a reductive carbonylation process of the nitroaromatic precursors directly, giving isocyanates (***g***) or carbamates (***h***, ***i***), the latter being subsequently cracked into isocyanate. For isocyanate producers, the advantages of these carbonylation processes starting from nitroaromatics were foreseen quite a long time ago and have accordingly attracted attention for more than 30 years. While an impressive amount of work has been conducted on these reactions or derived ones (like ***j***) under the stimulus of industry, publications of the results in academic journals was often delayed in time and sparse owing to the strategic importance of this research. Yet, among the wealth of publications that appeared continuously in the patent literature, the results reported are often misleading or conflicting, rendering their exploitation quite tedious. More significant mechanistic data became available in recent decades, concomitantly with the tremendous development of spectroscopic investigation means. With the hope of arousing more academic interest on these intriguing transformations, the purpose of the present article is to give to the reader a good overview of the present state of the art regarding the catalytic carbonylation of nitroaromatics using Group VIII transition metal catalysts. This work will be mainly based on academic publications, but the interested reader will find a more detailed coverage of the patent literature in the following related reviews[1] [57–63].

2. General notions

2.1. Reductive carbonylation of nitroaromatics; the direct and the indirect way

2.1.1. The direct carbonylation

The so-called ‘direct’ carbonylation is the direct formation of isocyanate from the corresponding nitroaromatic. Schematically, following the stoichiometry given in Eq. (1), the reaction takes place between one molecule of nitroaromatic and three molecules of carbon monoxide. It has to be conducted in an ‘innocent’ solvent, i.e. unreactive toward isocyanate, and the latter can be directly isolated from the reaction medium. This apparently simple reaction is in fact a complex multi-step transformation and despite a thermodynamic balance largely in favor of the products ($\Delta H° = -128.8$ kcal mol^{-1}), it requires the presence of a catalyst to proceed [64].

$$\text{Ar–NO}_2 + 3\text{CO} \rightarrow \text{Ar–NCO} + 2\text{CO}_2 \tag{1}$$

2.1.2. The indirect carbonylation

The ‘indirect’ carbonylation is a similar reaction conducted in the presence of a reactant able to form an addition compound with the isocyanate. Most often alcohol, as depicted in Eq. (2), is used for this purpose. We will call any

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[1] Notably, a book which covers quite exhaustively most of the patent literature relevant to this topic has been published while this manuscript was in preparation [56].

transformation that gives carbamates 'indirect carbonylation' from now on[2]. In order to obtain the desired isocyanate, de-alcoholysis (i.e. reverse of Eq. (3)) of the carbamate is needed. Thermal cracking, which allows quantitative recovery of the isocyanate, is usually used for large-scale production [81]. Other efficient 'top-bench' techniques exist for de-alcoholysis [82] and recently one of these has been proposed as a substitute for industrial thermal cracking [83].

$$\mathrm{Ar{-}NO_2 + 3CO + ROH \rightarrow Ar{-}NHC(O)O{-}R + 2CO_2} \tag{2}$$

$$\mathrm{Ar{-}NCO + R{-}OH} \xrightleftharpoons[\Delta]{} \mathrm{Ar{-}NHC(O)O{-}R} \tag{3}$$

Conceptually, the whole transformation given in Eq. (2) can be pictured as consisting of a direct carbonylation reaction (Eq. (1)), followed by a 'trapping' reaction of the isocyanate produced by the alcohol in a subsequent step (Eq. (3)). The latter is known to occur spontaneously at ambient temperature [84,85] and can be catalyzed by many compounds presenting either Lewis acidity or basicity [86–89]. Since this second reaction (Eq. (3)) is very much favored on thermodynamic grounds, the complete indirect carbonylation process (Eq. (2)) is even more exothermic than the direct one.

2.1.3. The nitroaromatic substrates used

For most of the investigations conducted on these reactions, simple mono-nitroaromatics were often chosen as a model substrates. However, it should be kept in mind that substrates allowing access to the industrially appealing aromatic poly-isocyanates like TDI or MDI (see Scheme 1) are poly-nitro aromatics. Whereas reactions of nitrobenzene can usually be extended to more complex aromatic substrates, it has been shown that with functionalized nitroaromatics, the nature and position of the substituents on the same aromatic ring will sometimes strongly influence the selectivity and yield of the transformation [6,62,63,90–94]. This is especially true for other nitro groups, and, in general, given a catalytic system, much harsher conditions are needed for total conversion of polynitro aryls relative to the corresponding mononitro substrates [63,95–98]. Consequently, attention has to be paid to the substrate used when comparing the efficiency of various catalytic systems.

Mechanically speaking, however, any carbonylation reaction of polynitro aryls is believed to proceed similarly to the mono-nitro substrates, but in a stepwise

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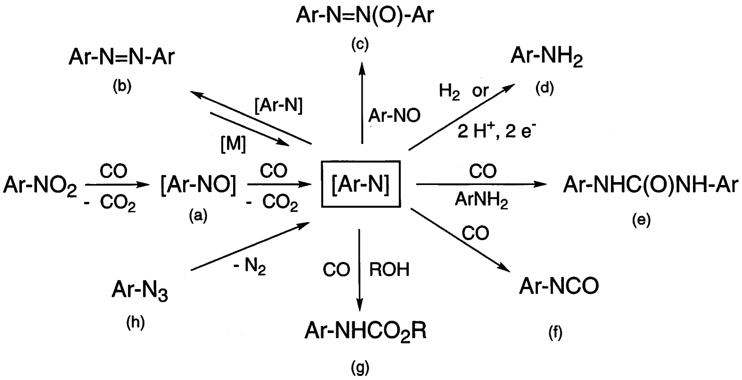
[2] When the reaction is conducted in presence of excess amine, ureas are similarly isolated (Scheme 2; ***j***). Compared to the reaction with alcohol, the $\Delta H°$ is now much decreased ($\Delta G°(298) = -7.5$ kcal mol^{-1}) [41] . This reaction also constitutes another type of indirect carbonylation [39,65–78]. When isocyanates are ultimately desired with such a reaction, the ureas formed have to be alcoholized first into carbamates [79] before being cracked into isocyanates afterwards. Indeed, the direct thermal cracking of ureas into isocyanates is a difficult process [16]. That does not render this reaction very advantageous over the typical alcohol-based indirect process. Moreover, the reaction mechanism of this transformation is unclear and perhaps more relevant from oxidative carbonylation of amines (Scheme 2; ***f***) [57,58]. Finally, the reaction where formate esters are used in place of alcohol (Scheme 2; ***i***) can also be considered as a derived indirect carbonylation [80]. Here again, for isocyanate production, the reaction presents no clear advantages over the typical indirect carbonylation in alcohols.

fashion, nitro-isocyanato aryls being formed as intermediates [63,95,96,98,99]. Thus, for the study of such transformations, the data extracted by use of mono-nitro aryls proves very informative and the logical approach when developing an active catalytic system for carbonylation of polynitro aromatics is often to test it first with simple nitroaromatic substrates. By this means, very efficient catalytic systems for direct or indirect carbonylation of dinitroaromatic substrates have been elaborated in the past few years (see Section 2.3).

2.2. Usual byproducts and related chemistry

Depending on the catalytical system used, many byproducts are usually formed in various proportions. We can distinguish different byproducts, those common to both direct and indirect carbonylation reactions (Eqs. (1) and (2)) and those more specific to one type of transformation. These products give some indirect information about complexes present in the medium with a particular catalytical system. In principle, they may all be generated from a common nitrene intermediate (see Scheme 3). In accordance with such a hypothesis, most of these byproducts are found in catalytical processes where such an imido-moiety is supposed to be transiently generated, such as the carbonylation of azides (h) or azo compounds (b) (see Section 4.2.1). Conversely, such transformations can be envisioned as other entries in this chemistry. We will now describe the typical families of byproducts usually isolated during nitroaromatic carbonylation and analyze their possible origin. Other more specific byproducts however have also been identified in specific indirect or direct carbonylation reactions [67,100,101].



Scheme 3.

2.2.1. Nitrosoaromatics

The nitrosoaromatics (a), result from incomplete deoxygenation of the starting nitroaromatic. In fact, those products are seldom isolated, since they are more prone to further reduction (deoxygenation) than the initial nitro substrate [90,102,103].

2.2.2. *Azo- and azoxyaromatics*

More important common byproducts, especially in non-protic reaction media, are the azo- and azoxyaromatics (b, c). With palladium catalysts, azobenzenes were envisioned many times as possible intermediates in the catalytical transformation [104,105], however these suppositions were always disproved [104,106–108]. Moreover, at high concentration, they were even reported to poison the catalyst [109]. Formally, those products appear to result from the coupling of an imido precursor with itself or with some nitroso byproduct [110–112] and as such, have often been invoked as evidence for the formation of a metal–imido species during the carbonylation process. More uncommon pathways, not involving any nitrene precursor, can however also be devised for their formation (Eqs. (4)–(7)):

$$\mathrm{Ar{-}N{=}N(O){-}Ar + CO \rightarrow Ar{-}N{=}N{-}Ar + CO_2} \tag{4}$$

$$\mathrm{Ar{-}NO + ArNCO \rightarrow Ar{-}N{=}N{-}Ar + CO_2} \tag{5}$$

$$\mathrm{Ar{-}NO + ArNH_2 \rightarrow Ar{-}N{=}N{-}Ar + H_2O} \tag{6}$$

Thus azo compounds could be formed upon 'de-oxygenation' from azoxy byproducts (Eq. (4)) [102,104] or by coupling of the transient nitroso byproduct with other potential products or byproducts of the reaction such as isocyanate or amine (Eqs. (5) and (6)) [113,114], while azoxyaromatics could simply result from (metal-assisted) disproportionation of a nitroso intermediate following Eq. (7) [115]:

$$\mathrm{3Ar{-}NO \rightarrow Ar{-}NO_2 + Ar{-}N{=}N(O){-}Ar} \tag{7}$$

2.2.3. *Amines*

Whereas the previous byproducts were quite common, amines (d) usually constitute one of the main side products in indirect carbonylation processes. They are believed to result from the protonation of some metal–imido intermediate by protons resulting, either from an acidic promoter present in the medium [91], or from adventitious traces of water [100,116–121]. Molecular hydrogen generated in situ from water traces by the water-gas shift reaction, has however been disproved in many cases as being the hydrogen source for substrate reduction in nitroaromatic carbonylation reactions [122]. Likewise, the possibility that amine would be generated upon hydrolysis of the isocyanate produced by water traces has also been disproved (Eq. (3), $R = H$) [118,123]. Quite recently, aniline was proposed not to be a side-product in the reductive carbonylation of nitroaromatic compounds, but rather an active intermediate, for certain Ru-, Rh- and Pd-based indirect systems (see Sections 3.2 and 4.3.3).

2.2.4. *Ureas and biurets*

In general ureas (e) or biurets are found in direct carbonylations, when free amine was present in the medium. These are possibly formed by the condensation of, respectively, amine or urea, with the catalytically formed isocyanate (Eqs. (8) and (9)) [16,86,124]. Although this reaction usually occurs spontaneously, it could also happen in the coordination sphere of the transition metal complex present in the medium [125,126]. While reaction (9) is reversible at high temperatures [127,128], the quantitative reversal of Eq. (8) is much more difficult to achieve, pyrolysis of the urea giving isocyanates only in specific cases [16].

$$\text{Ar–NCO} + \text{Ar–NH}_2 \rightarrow \text{Ar–NHC(O)NH–Ar} \qquad (8)$$

$$\text{Ar–NCO} + \text{Ar–NHC(O)NH–Ar} \rightarrow \text{Ar–NHC(O)N(Ar)C(O)NH–Ar} \qquad (9)$$

Despite the fact that reaction (8), even unpromoted, occurs much faster than the similar condensation between an isocyanate and an alcohol (Eq. (3)), ureas or biurets are seldom observed as final products in the presence of alcohol. Indeed, carbamates are favored on thermodynamic grounds and it has been demonstrated in many instances that ureas or biurets were alcoholyzed in carbamates under catalytical conditions, even in the absence of the catalyst (Eq. (10)) [35,43,46,70,100,121,129]:

$$\text{ROH} + \text{Ar–NHC(O)NH–Ar} \rightarrow \text{Ar–NHC(O)OR} + \text{Ar–NH}_2 \qquad (10)$$

As a consequence, when ureas are characterized at the end of catalytic runs where alcohol is present in excess, their occurrence as products arising from minor side-reactions is questionable. Typically in related oxidative carbonylation of amines processes, under such circumstances, they were strongly suspected to be reaction intermediates [15,44,68]. More recently urea was even proposed to constitute a true organic intermediate in an indirect carbonylation process catalyzed by ruthenium complexes (see Section 3.2.2).

2.2.5. Isocyanate oligomers

Isocyanate oligomers like uretediones ($n = 2$) or isocyanurates ($n = 3$) are quite specific to direct carbonylation processes. They are probably formed either by assisted or spontaneous self-coupling reactions (Eq. (11)) of the isocyanate which accumulates in the medium (see Section 5.2) [86,130,131]:

$$n\,\text{Ar–NCO} \overset{\text{(Cat.)}}{\rightleftharpoons} (\text{Ar–NCO})_n \qquad (11)$$

2.3. Catalytic systems for reductive carbonylation

2.3.1. Historical background

The use of carbon monoxide for reduction of nitrogen–oxygen aromatic bonds was initially reported in 1949 by Buckeley and Ray who converted nitrobenzene in azobenzene under very harsh conditions (250°C, 3000 bar), forming carbon dioxide [132]. Following this discovery, it was rapidly stated that transition metal carbonyl complexes could promote this transformation under much milder conditions [133–136]. This initiated research on various reduction processes of the nitroso aromatic linkage assisted by transition metal complexes using carbon monoxide atmosphere as oxygen acceptor [137]. Subsequently, in 1967, Hardy and Bennett reported the catalytical generation of isocyanates from nitro compounds using rhodium, palladium or other noble metal salts in the presence of a Lewis acid promoter [138].

Catalytic systems comprising various transition metal salts were then systematically tested for this transformation. Up to now, the more interesting results owing to industrial applications were obtained with Group VIII metal catalysts. Selenium compounds were often reported to very efficiently catalyze this transformation [59,139], but these derivatives appear far too toxic to be usable in any industrial application, whereas other catalysts often investigated such as sulfur [140–142] or copper [62,143] exhibit only moderate activity in regard to the turnover achieved by active Group VIII catalysts. We will now focus on the latter.

The catalytic system typically consists of a catalyst precursor used in conjunction with various promoters. These can either be ligands, either co-catalysts (most often Lewis acids) or both. Homogeneous or heterogeneous precursors were usually employed, regardless of the real nature of the catalytic intermediates (see Section 4.1.1). Most often, the catalytic system was a mixture of a given metal salt or a supported metal with ligands able to generate the active species in situ. Alternatively, pre-formed homogeneous complexes of the ligand were also used as efficient catalysts. In general, Lewis acidic co-catalysts are not needed for the catalysis to proceed, but often allow dramatic increase in the yield of the desired product. Thus, the selectivity and conversion of a the carbonylation reaction is strongly dependent on the nature and proportions of the precursor–ligand–promoter triad, as well as on the temperature and carbon monoxide pressure applied during the reaction. Typical reaction temperatures range between 120 and 200°C, whereas pressures usually lie between 40 and 100 bar. Some selected examples of catalytic systems which have been studied in various articles are given in Tables 1 and 2 and the corresponding turnover numbers calculated, whenever possible. It must however be emphasized that higher activities may apparently be achieved with some of these, or variants thereof, under the optimal conditions usually reported in patents. Therefore, caution should be used when using these data for strict comparison purposes. Finally, another point which is immediately apparent from Tables 1 and 2 is the fact that few of the catalytic systems known have been investigated with di- or polynitroaromatic substrates.

2.3.2. Direct carbonylation

For direct carbonylation of mono- or di-nitroaromatic compounds, simple heterogeneous catalyst precursors such as Rh/C or Pd/C [139,143] were poorly active. Inorganic polymeric precursors like $RhCl_3$ and $PdCl_2$ were also reported[3] to give poor results [63]. The presence of a Lewis acid promoter strongly increases the rate of the reaction and also enhances the selectivity toward isocyanate [95,107,151,152,161,162]. For instance, the ($[Rh(CO)_2Cl_2]/MoCl_5/VCl_4$) system is active even under 1 atm of carbon monoxide [92]. Unfortunately, in spite of its high activity, this catalyst deactivates quite rapidly and only a moderate turnover is achieved for longer reaction times (see Table 1). Addition of an aromatic amine

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[3] Note that, it has been demonstrated that some of these crude salts were able to extract metals from the reactor walls and these may act as in situ-generated cocatalysts and promote the reaction [106,160]. Therefore, the activity initially reported for the crude salts may be questionable.

Table 1

Catalytic systems for direct carbonylation of nitrobenzene or of 2,3-TDI to the corresponding mono- or diisocyanate

Catalytic system	Solvent	Time (min)	Temperature (°C)	Pressure (bar)	Conv.[a] (%)	Sel.[b] (%)	Ton[c] (h^{-1})	Ref.
Mononitroaromatic substrates								
$Ru_3(CO)_{12}$	CH_3CN	180	140	22	40	94	2	[144]
$[HRu_3(CO)_{12}]^-$	CH_3CN	180	140	22	100	95	5	[144]
$Ru_3(CO)_{12}$–3dppe	Toluene	300	170	60	35	>1	≤ 1	[145]
Rh(5%)/C–$FeCl_3$	Benzene	330	190	500	100	35	≥ 5	[138]
$Rh_6(CO)_{16}$–3bipy	Toluene	90	170	60	22	24	7	[145]
$[Rh(CO)_4](PPN)$–8bipy	Toluene	300	170	60	4	0	0	[102]
$[RhCl(CO)_2]_2$–$MoCl_5$	ODCB	30	100	1	50[d]	52[d]	5[d]	[146]
$[RhCl(CO)_2]_2$–8Py · HCl–25Py	CB	60	185	50	60	71	29	[147]
$[RhCl(CO)_2]_2$–5Py · HCl–20Py	CB	60	205	50	100	90	60	[147]
$(PPh_3)_2Rh(CO)H$–$MoCl_3$	CB	60	25	80	17	100	2	[93]
$(PPh_3)_2Rh(CO)H$–$MoCl_3$	CB	60	25	80	100[f]	100[f]	10[f]	[93]
Rh(10%)/Al_2O_3	ODCB	400	200	240	100	70	≥ 18	[148]
$(PPN)_2RuRh_4(CO)_{16}$–8bipy	Toluene	300	170	20	21	27	≥ 1	[102]
$PdCl_2$	CH_3CN	600	225	100	100[e]	15[e]	150[e]	[149]
$PdCl_2$–V_2O_5–4Py	/	120	200	100	100[e]	92[e]	122[e]	[150]
$PdCl_2$–20$(PyH)_2Fe_2Cl_8(Py)_2$	ODCB	240	250	17	83[d]	84[d]	175[d]	[151]
Pd/Ba_2SO_4–20$(PyH^+)_3Fe_2Cl_9$	ODCB	240	235	24	48[d]	97[d]	117[d]	[151]
$PdCl_3(CO)(NBu_4)$–VCl_3 · 3THF	ODCB	30	120	1	98[f]	96[f]	28[f]	[152]
'Pd_2Mo_2' cluster/Al_2O_3–30Py	ODCB	72	240	200	100	71	86	[153]
$Pd(Py)_2Cl_2$	CB	120	200	100	20	72	9	[154]
$Pd(Py)_2Cl_2$–3V_2O_5	CB	240	190	78	31	90	7	[155]
$[Pd(TMB)_2]_3$–tmphen–24TrMBA	Benzene	120	180	40	47	71	21	[156]
$[Pd(OAc)_2]_3$–2tmphen–24TrMBA	Benzene	120	180	40	41	74	19	[156]
$Pd_{561}(phen)_{60}(Oac)_{180}$–$XsBrNMe_4$	/	180	150	150	/	12[i,k]	22[i]	[157]
$Pd_{561}(phen)_{60}(Oac)_{180}$–$XsBrNMe_4$	PhOH	180	150	140	/	24[i,k]	45[i]	[157]
$Pd(NH_3)_4Cl_2$–0.5$H_3PMo_{12}O_{40}$	DME	180	170	41	19	95	6	[158]
Pd(5%)/Al_2O_3–2tmphen–24TrMBA	Benzene	120	180	40	43	53	14	[156]

Table 1 (*Continued*)

Catalytic system	Solvent	Time (min)	Temperature (°C)	Pressure (bar)	Conv.[a] (%)	Sel.[b] (%)	Ton[c] (h^{-1})	Ref.
Dinitroaromatic substrates								
$Rh(Py)_3Cl_3$	CB	240	195	85	100	$48/80^{g}$	4	[159]
$Pd(Py)_2Cl_2$–$10Fe_2O_3$–$FeVO_4$	ODCB	180	260	330	100	90	6	[97]
$Pd(Py)_2Cl_2$	CB	120	195	85	82	$22/99^{g}$	3	[159]
$Pd(Py)_2Cl_2$–$3V_2O_5$	CB	120	195	85	89	$27/98^{g}$	4	[159]
$PdCl_2 + 4Py$	CB	240	195	85	100	55	3	[159]
$PdCl_2$–4Py–MoO_3–$2Fe_2O_3$	ODCB	120	170	300		$90^{k}/90^{k,g}$	9	[95]
$PdCl_2$–Py–MoO_3–$2Fe_2O_3$	ODCB	120	200	125	100	$58/58^{g}$	6	[96]
$PdCl_2$–5Py–MoO_3–$2FeCl_3$	CB	60	190	200	98	$67/94^{g}$	56	[160]
$Pd(isoqin)_2Cl_2$–$1.2Fe(MoO_4)_3$	ODCB	90	195–206	200	99	$68/73^{g}$	12	[99]
Pd(Phen)DBA	ODCB	20	120–130	200	23	$0.15/3^{g}$	0.5	[99]
$(6PdO$–$2MoO_3$–$Fe_2O_3)/Al_2O_3$–110Py	ODCB	120	210	300	/	$55^{k}/70^{k,g,j}$	55^{j}	[94]

[a] Conv. = percentage of reacted substrate.

[b] Sel. = percentage of carbamate on reacted substrate.

[c] Ton = turnover number in mol of product per mol of catalyst per h, times (×) the number of nitro functions in the substrate for polynitroaromatics.

[d] *para*-Nitrotoluene used in place of nitrobenzene.

[e] *para*-Chloronitrobenzene used in place of nitrobenzene.

[f] 2,4,6-Nitromesitylene used in place of nitrobenzene.

[g] Total selectivity for isocyanate-containing compounds.

[h] Ton per mol of cat. present and yield rel. to [Pd] in the catalyst.

[i] Calculated for a 10% Pd containing catalyst.

[j] Yield of product (= Conv. × Sel.).

Table 2
Catalytic systems for indirect carbonylation of nitrobenzene or of 2,3-TDI to the corresponding carbamate or dicarbamate

Catalytic system	Solvents	Time (min)	Temperature (°C)	Pressure (bar)	Conv.[a] (%)	Sel.[b] (%)	Ton[c] (h^{-1})	Ref.
Mononitroaromatic substrates								
$Ru_3(CO)_{12}$	Toluene–MeOH	300	170	60	36	22	3 (400)	[121]
$Ru_3(CO)_{12}$	MeOH	1320	160	70	/	68[j]	4	[178]
$Ru_3(CO)_{12}$	EtOH	275	160	70	/	7[j]	2	[179]
$Ru_3(CO)_{12}$–$7NEt_4Cl$	Toluene–MeOH	300	170	60	100	93	6	[121]
$Ru(PPh_3)_2(CO)_3$–$20NEt_4Cl$	Toluene–MeOH	420	170	60	100	85	12	[121]
$Ru_3(CO)_{12}$–4bipy	Toluene–MeOH	90	170	60	100	82	55	[145]
$Ru_3(CO)_{12}$–3dppe	Toluene–MeOH	180	170	60	90	60	36	[145]
$Ru(saloph)Cl_2$	MeOH	420	160	15	/	/	82	[180]
$Ru(dppe)(CO)_3$	*o*-Xylene–MeOH	600	145	75	96	86	4[d]	[120]
$Ru(phpy)(CO)_2Cl$–13NaOMe	DMSO–MeOH	360	150	90	100	80	15	[181]
$Rh_6(CO)_{16}$–3bipy	Toluene–MeOH	90	170	60	88	81	95	[145]
$Rh_6(CO)_{16}$–3dppe	Toluene–MeOH	90	170	60	42	24	13	[145]
$(PPN)_2Rh(CO)_4$–1.5bipy	THF–MeOH	90	170	60	61	68	68	[102]
Rh(5%)/Al_2O_3–1.5bipy	Toluene–MeOH	180	200	100	61	68	28	[156]
$Rh(Py)_3Cl_3/Al_2O_3$–$19FeCl_3$	MeOH	300	165	100	99	98	80	[182]
$[(PPh_3)_2Rh(OH)]_2$–Bipy	Benzene–MeOH	960	180	70	/	94[j]	6	[183]
$(PPh_3)_2Rh(CO)Cl$–$15FeCl_3$	MeOH	20	180	60	/	29[j]	20	[184]
$(PPh_3)_2Ir(CO)H$–$15FeCl_3$	MeOH	20	180	60	/	10[j]	7	[184]
$(PPN)_2RuRh_4(CO)_{16}$	THF–MeOH	90	170	60	82	66	36	[102]
$(PPN)_2FeRh_4(CO)_{16}$–8bipy	THF–MeOH	90	170	60	44	44	48	[102]
$(PPN)_2RuRh_4(CO)_{16}$–8bipy	THF–MeOH	90	170	60	98	88	57	[102]
$(PPN)_2OsRh_4(CO)_{16}$–8bipy	THF–MeOH	90	170	60	100	89	≥ 59	[102]
$NiI_2(PPh_3)_2$	EtOH	780	180	40	50	10	≤ 1	[68]
PdO–2Py	EtOH	120	200	120	50	10	1	[185b]
PdO–2Py–$2FeCl_3$	EtOH	120	200	120	73	57	10	[185b]
$PdCl_2$–180Py–$2FeCl_3$	EtOH	60	180	20	40	37	34	[186]
(10%)$PdCl_2$/NaX–200Py–$13FeCl_3$	EtOH	60	180	120	47	43	30	[186]
$PdCl_2$–$0.5H_3PMo_{12}O_{40}$	DME–MeOH	180	150	40	84	97	27	[158]
$Pd(pic)_2(OAc)_2$–$25FeCl_3$	MeOH	300	200	40	61	/	≤ 93	[37]
$[Pd(OAc)_2]_3$–70 phen–30*p*-TSA	DMP–MeOH	120	135	60	88	75	660	[109]

Table 2 (*Continued*)

Catalytic system	Solvents	Time (min)	Temperature (°C)	Pressure (bar)	Conv.[a] (%)	Sel.[b] (%)	Ton[c] (h^{-1})	Ref.
$[Pd(OAc)_2]_3$–3phen–8TFA	EtOH	30	180	120	100	90	972	[119]
(phen)$Pd(Oac)_2$–$4CuCl_2$	MeOH	600	200	30	45	100	5	[187]
$[Pd(OAc)_2]_3$–70phen–Ag(Oac) –30*p*–TSA	DMP–MeOH	120	135	60	94	78	733	[109]
$[Pd(tfa)_2]_3$–70phen–Ag(tfa) –30*p*-TSA	DMP–MeOH	120	135	60	95	83	788	[109]
$[Pd(OAc)_2]_3$–6dmphen–3*p*-TSA	MeOH	120	135	80	82	85	255	[188]
$Pd(phen)_2(OTf)_2$–4phen	CB–MeOH	/	135	60	/	84	234	[189]
$Pd(tmphen)_2(PF_6)_2$	EtOH	120	180	40	100	95	≥59	[190]
$Pd(dmphen)_2(BF4)_2$–4dmphen	MeOH	120	135	80	86	86	271	[188]
$Pd(dmphen)_2(OTf)_2$–4dmphen	MeOH	120	135	80	100	84	311	[188]
Pd/bipy/Clay–$20FeCl_3$–66Py	Toluene–MeOH	330	170	60	98	78	14	[191]
$Pd(Ph_3P)_2Cl_2$–dppp–$1.5K_2CO_3$	Benzene–MeOH	1440	160	20	100[e]	89[e]	2[e]	[192]
$Pt(PPh_3)_2Cl_2$–10 $SnCl_4$–$40NEt_3$	EtOH	240	180	60	97	86	42	[193]
Pd(5%)/C–tmphen–8TrMBA	EtOH	120	180	40	99	95	59	[194]
Pd/Clay–$Ru_3(CO)_{12}$–bipy	Benzene–MeOH	720	180	70	≥97[e]	?	20[e]	[76]
Dinitroaromatic substrates								
$Ru_3(CO)_{12}$–$6.5NEt_4Cl$	Toluene–MeOH	420	170	60	100	50	2	[121]
$Pd(tmphen)_2(OAc)_2$–8TrMBA	EtOH	120	180	40	100	90	112	[208]
$[Pd(OAc)_2]_3$–7 phen–14TMBA	MeOH	10	135	60	100	85	663	[119]
$Pd(phen)_2(OTf)_2$–4phen	CB–MeOH	120	135	60	23	63[f]/100[h]	61[f,g]/78[g,h]	[189]
$Pd(phen)_2(OTf)_2$–4phen–100*p*-CBA	CB–MeOH	300	135	60	/	86[f]/98[i]	73[f,g]	[189]
$Pd(dppp)Cl_2$–$1.5K_2CO_3$	Benzene–MeOH	350	160	20	/	59[f,j]	≥2[f]	[192]
Pd/Clay–$1.5Ru_3(CO)_{12}$–25bipy	Benzene–MeOH	720	180	70	/	75[j]	31	[76]
Pd/Clay–$1.5Ru_3(CO)_{12}$–25bipy	Benzene–MeOH	1480	180	70	/	96[j]	40	[76]

[a] Conv. = percentage of reacted substrate.

[b] Sel. = percentage of carbamate on reacted substrate.

[c] Ton = turnover number in mol of product per mol of catalyst per h, times (×) the number of nitro functions in the substrate.

[d] Unoptimized conditions reported for this system.

[e] *para*-Nitrotoluene used in place of nitrobenzene.

[f] *para*-Dinitrobenzene used in place of TDI.

[g] Ton based on nitro substrate (and not product) here.

[h] *para*-Carbamato-nitrobenzene used in place of TDI.

[i] Total selectivity for carbamate-containing compounds.

[j] Yield of product (= Conv. × Sel.).

ligand such as pyridine is also very effective with most of the metal chlorides [37,92,94,97,147,152,159,162–175]. The promoting ability of the Lewis acid promoter was often less pronounced in systems comprising good ligands [63]. Clearly, when using simple metal salts as catalyst precursors, a careful choice of the other components of the triad can lead to very efficient catalytic systems, active even for dinitroaromatic substrates [63,95,96,98,99,176].

Polymetallic carbonyl precursors were also claimed to be catalysts [144]. For isocyanate production, $Ru_3(CO)_{12}$ or $[HRu_3(CO)_{12}]^-$ are however moderately active with nitrobenzene in acetonitrile [144], and proved completely inactive in many other solvents or with other substrates [67,101,121,177], urea usually being the main product formed in these cases. Screening of various promoters or ligands did not greatly increase the yield of isocyanate (Table 1).

Finally, mention should also be made here of quite active Pd-based systems discovered lately. One ([Pd]/phen/H^+) associates a chelating diimine ligand and non-coordinating carboxylic acids like 2,4,6-trimethylbenzoic acid (TrMBA) with a homogeneous palladium(II) precursor [156], while the other is the combination of an heteropolyanion with a palladium source in the presence of chloride ions ([Pd]/Cl^-/HPA) [158]. These systems constitute, however, much better catalysts for indirect carbonylations.

2.3.3. Indirect carbonylation

For indirect carbonylation processes, very similar catalytic systems could be used to catalyze the transformation. Metals deposited on various solid supports in presence of ligands [76,182,185,191,196], or systems as (MX_n/ligand/Lewis acid) with $RhCl_3$ or $PdCl_2$ were active [6,168,185b,186]. New catalytic systems with iridium [197] or platinum complexes preformed as precursors like $PtCl_2(PPh_3)_2$/$SnCl_4$ were also effective [193,198].

Polynuclear precursors like carbonyl clusters of rhodium or ruthenium constituted much more active catalysts for carbonylation, especially when used with a co-catalyst like NEt_4Cl [121,199]. The presence of a chelating ligand also had a tremendous effect on their activity, and this gave rise to the generation of very active systems based on chelating ligands and homogeneous metal precursors (Table 2). The presence of a co-catalyst was essential for the catalysis to proceed efficiently and specifically, for instance a diimine ligand was required with Pd-based catalysts[4]. Attempts to replace the diimine by a diphosphine ligand or vice-versa in these systems often resulted in lower selectivity and lesser yields [119,192]. Among all these new systems, ([Ru]/dppe) [120,178,202–206], ([Rh]/phen) [112,156] or ([Pd]/phen/H^+) [76,190,194,195,199,207–210] systems have been more thoroughly studied than the others. Very impressive results are obtained in the last case, even when the Brönsted acid co-catalyst is replaced by a cerium(IV) salt [211,212]. Fine

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[4] Typically, phosphine-type ligands proved usually deceptive in these transformations unless an aromatic amine like aniline was present [75,77,200,201]. In such cases, however, the mechanism of the reaction appear to proceed differently, i.e. by oxidative carbonylation of the amine (see Section 4.3.3) [58,77].

electronic [100,188,213] or steric [119] tuning of the diimine ligand permit optimization of the yields in carbamate. Other recently discovered active catalysts are ruthenium complexes of Schiff bases [180] or systems associating palladium salts with Keggin-type heteropolyanions ($PdCl_2$/HPA) [158,176,214,215]. Interestingly, among these new catalysts many are based on available non-chlorinated metal precursors or co-catalysts and readily accessible chelating ligands [90,91,100,156,188,194,216]. This is important in view of the requirements needed for eventual industrial exploitation (see Section 5.1).

3. Proposed mechanism for reductive carbonylation

For a long time, stimulated by industry, research was essentially aimed at improving the existing catalysts or finding new more active ones. Apart from some mechanistic proposals, only scant information was available in the literature on the reaction mechanisms for these, mostly due to the reaction conditions making any in situ observation of the intermediates by the usual spectroscopic means difficult. As late as 1988, and despite intense activity in this field, the lack of mechanistic insight in catalytical reactions underlying those transformations was noted by several authors [62]. Only after 1988, with the emergence of more performant techniques, were in-depth studies performed on the most active catalysts [143]. These gave reliable insight into the mechanistic features, disproved some of the old assumptions and raised new questions. We will now review mechanisms proposed for most of the various direct and indirect catalytic systems investigated.

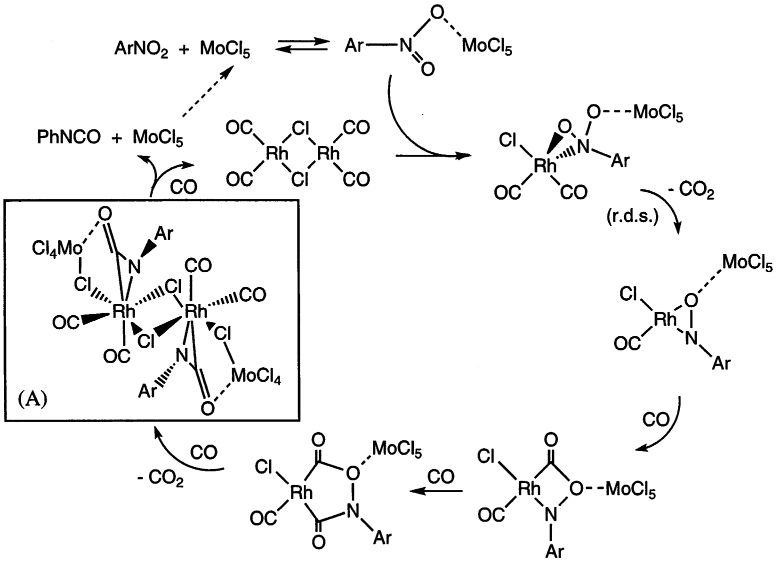
3.1. Direct carbonylation

As shown in Scheme 3, carbonylation of nitroaromatics was initially pictured as being a stepwise deoxygenation of the nitro group, yielding a nitrene (probably stabilized by coordination on a metal center), which is finally carbonylated to yield the isocyanate (f) or the carbamate (g) in the presence of alcohol [217]. This simple mechanism involving a metal–imido intermediate as key intermediate was a common feature of most of the mechanisms proposed after the work of Weigert et al. with $PdCl_2$ in 1973. By use of labeled nitro substrates, he showed that the formation of a transient nitrene species could easily rationalize the observed ratios of isolated products in this transformation (see Scheme 3) [149]. However, the real nature and the nuclearity of the reaction intermediates was not discussed in his report.

3.1.1. The ($RhCl_3$/$MoCl_5$) system and related systems

In 1977, studying the system $RhCl_3$/$MoCl_5$, Schwetlick et al. proposed a very different mechanistic interpretation from the commonly accepted working hypothesis. Their catalytic cycle involves mononuclear metal complexes as intermediates (see Scheme 4) [146,218,219].

Due to the low pressure of carbon monoxide required for the reaction to proceed (1 atm), the kinetics of the transformation could be monitored by IR. The reaction



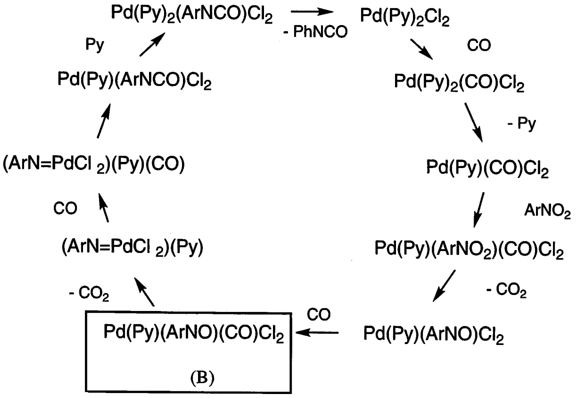
Scheme 4.

rate was first order relative to nitro substrate, half order relative to the dimeric catalyst precursor, first order relative to the co-catalyst and zero order relative to carbon monoxide [218a]. Accordingly, the rate determining step (r.d.s.) of the catalytic cycle was supposed to be the first deoxygenation of the nitroaromatic [218b]. Rate–temperature dependence gave $\Delta H^{\neq} = 18$ kcal mol^{-1} and $\Delta S^{\neq}_{373\mathrm{K}} = -30$ cal mol^{-1} K^{-1} for this step. On the basis of the various reaction rates found with different substrates, the activation of the nitro group was proposed to be initiated by electron transfer from catalyst. Nitroaryls having a non-coplanar nitro group (*ortho* substituents) reacted faster than others. An ill-characterized dinuclear rhodium isocyanate complex (A) containing the molybdenum Lewis acid was also isolated. The promoting effect of the $MoCl_5$ co-catalyst was tentatively explained by its coordination to one of the oxygen atoms of the nitro substrate during the transformation, thereby facilitating deoxygenation or carbon monoxide insertion [218b,219]. Independently, it has been proposed that the promoting role of $MoCl_5$ was to favor the dissociation of the dimeric rhodium precursor [220]. Even if highly speculative, this mechanism was quite new in the sense that it did not involve a metal imido intermediate [221–223].

With the related system ($[Rh(CO)_2Cl]_2/Py \cdot HCl$) studied by Nefedov et al., half order dependence on dinuclear catalyst, first order on starting nitroaromatic but inverse order dependence on carbon monoxide was found [147,172,220]. This further suggests that the actual catalytic species in both systems are mononuclear intermediates and that the r.d.s. is related to the nitro activation.

3.1.2. The (Py_2PdCl_2/Py) and related systems

In 1986, Chaudhari et al. studied the complex $Pd(Py)_2Cl_2$ as the catalyst in a similar transformation [154,155,159]. This study has precedence in prior independent work effected by Russian researchers [94,150,163,169,171,224]. Added Lewis acids had apparently only moderate beneficial effects on this particular system when an excess of pyridine was present. It was also suggested that the promoting role stated for the pyridine ligand was to keep the metal in solution as a monomeric form since inactive metal-containing polymers were formed in its absence [63]. Chaudhari et al. also managed to isolate an unstable and ill-characterized solid believed to be the nitroso complex $(Py)(CO)[m\text{-}(ClC_6H_4)NO]PdCl_2$ (B) which was proposed to be an intermediate in the transformation [154]. Based on the common assumption that the reaction proceeded by formation of a nitrene intermediate, they proposed a conventional mechanism for the reaction with mononuclear homogeneous intermediates (see Scheme 5). From the pressure drop versus time in a run without co-catalyst, the rate law of the reaction could be determined and showed apparent first order dependence in carbon monoxide and catalyst concentration, but zeroth order in nitro substrate. The activation energy found for the total process was 13.27 kcal mol^{-1} [155].



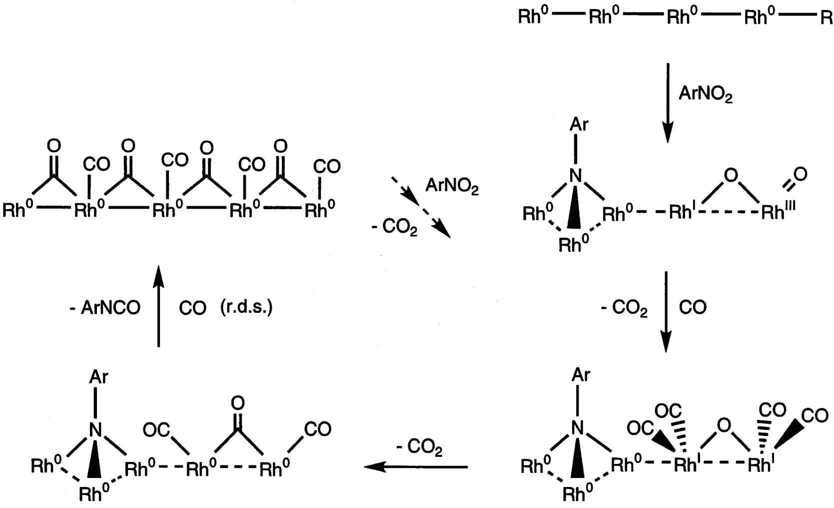
Scheme 5.

Quite simultaneously, kinetic investigations for the related ($[Pd(CO)Cl_3](NBu_4)$/$VOCl_2 \cdot 2THF$) system featuring no heteroaromatic ligand were established by Schwetlick et al. [152]. First order dependence in catalyst, co-catalyst and carbon monoxide, and zero order for nitroaromatic were found in the r.d.s. Rate–temperature dependence gave $\Delta H^{\neq} = 34$ kJ mol^{-1} and $\Delta S^{\neq}_{373\ K} = -233$ J mol^{-1} K^{-1} for this step. Here, no precise mechanism was given, since it was stated that these data were equally compatible with metal–imido or metallacyclic intermediates.

Thus, in opposition to the previously described Rh-based systems, it appears that the r.d.s. in Pd-based systems is independent of nitroaromatic concentration. This suggests that it is a step after activation of the nitro group on the catalyst and involves an interaction with external CO, such as perhaps oxygen insertion in a carbonyl ligand (first order dependence in CO).

3.1.3. The ($Rh/Al_2O_3/Py$) system

Even though heterogeneous catalyst precursors were previously used, to the best of our knowledge, a purely heterogeneous mechanism was never advanced until the work of Elleuch et al. in 1982 [148]. Using a supported heterogeneous rhodium precursor to effect the direct carbonylation in pyridine, these researchers observed various species coordinated on the rhodium(0) surface by means of infrared spectroscopy. These were proposed to be intermediates in the reaction process and a mechanism involving metal–imido surface species was proposed (see Scheme 6).



Scheme 6.

The r.d.s. of the reaction is believed to be the insertion of carbon monoxide into the surface-coordinated imido ligand. This mechanism is distinct from the previous proposals in the sense that deoxygenation of the nitro involves transient formation of metal–oxo species. Despite the fact that pyridine constitutes a good ligand for rhodium, the possibility of metal-leaching from the support under the reaction conditions was not discussed[5].

3.1.4. $Ru_3(CO)_{12}$ and other cluster-derived systems

For a time, only mononuclear intermediates had been postulated in homogeneous reaction schemes. However, polynuclear carbonyl complexes were known to stabilize reactive ligands as imido moieties by multiple coordination to their cluster core and it had also been established that imido-clusters could be generated from nitroaromatics by carbonylation reactions [225–229]. In this respect clusters became particularly attractive as possible intermediates in the reaction schemes. In

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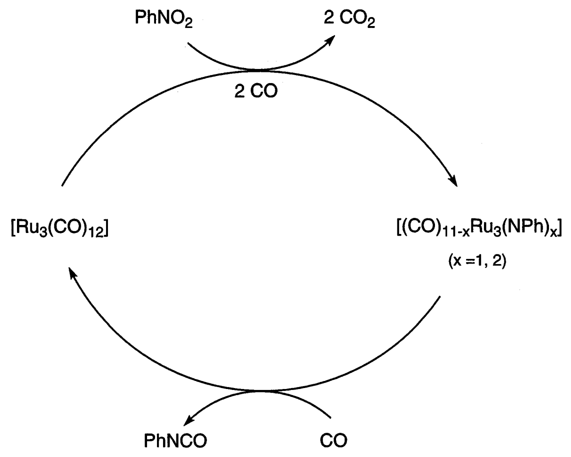
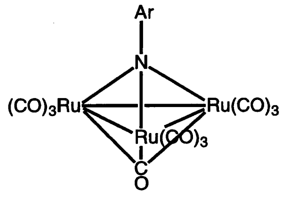
[5] It has recently been suggested that the reaction cycle might have been performed by traces of an homogeneous species [56]. As noted earlier, pyridine is commonly used as a ligand for rhodium in homogeneous direct systems [63,159]. See also [182].

1987, a homogeneous mechanism with polynuclear intermediates was proposed for the direct carbonylation by Bhaduri et al. using the $Ru_3(CO)_{12}$ cluster as catalyst precursor (see Scheme 7) [144,230].

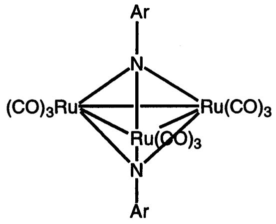


Scheme 7.

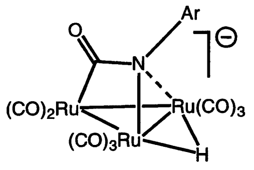
In that study, the imido trinuclear clusters $Ru_3(CO)_{10}(NPh)$ (C) and $Ru_3(CO)_9(NPh)_2$ (C′) were isolated from the reaction medium. The cluster (C) which was believed to be an intermediate in the process had already been structurally characterized [231]. The mechanism proposed was again classical, involving a metal–imido intermediate.



(C)



(C′)



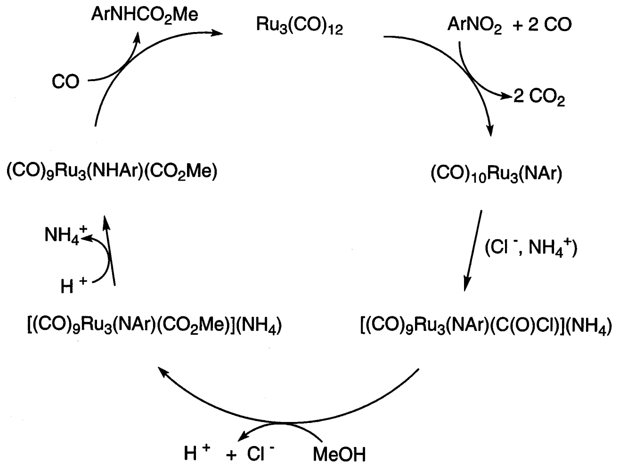
(D)

In 1988, a ruthenium cluster containing a π-ligated PIC ligand (D) was synthesized and structurally characterized by Bhaduri's group [232]. Its involvement as an intermediate in the catalytic cycle was claimed, but could, however, not be conclusively established [233]. The real intermediacy of polynuclear species in such processes was questioned in many instances and is still a matter of debate [177]. The simultaneous occurrence of two catalytic pathways involving low nuclearity and high nuclearity aggregates has even been proposed in a closely related reaction [234]. Finally, such a mechanism does not explain the apparent strong dependency of the isocyanate selectivity stated, on the solvent or substrate used [67,101,121,177].

3.2. Indirect carbonylation

3.2.1. ($Ru_3(CO)_{12}$/TBACl) and other cluster-derived systems

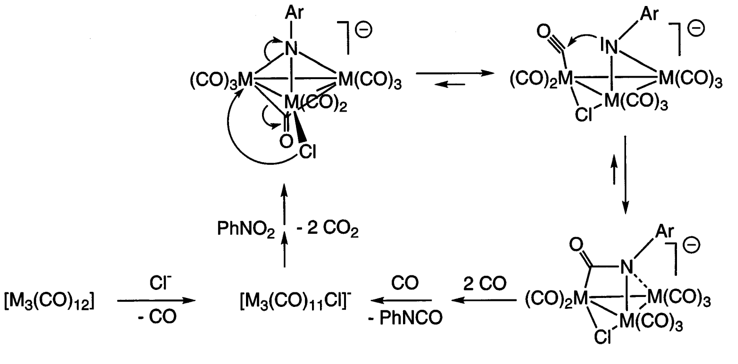
The polynuclear $Ru_2(CO)_{12}$ proved to be much more active for carbamate generation, especially when used with tetrabutylamonium chloride (TBACl). Conversely, ($Ru_2(CO)_{12}$/TBACl) was quite inactive for isocyanate production when alcohol was omitted and gave mainly ureas [67,101,121,235]. This indirect system was studied by Cenini et al. in 1984 [199] and 1988 [121]. Regarding previous proposals made for the direct transformation (see Section 3.1.4), an original mechanism involving polynuclear species was proposed. These researchers could confirm that deoxygenation of nitroaromatic substrates by carbon monoxide was a general route toward imido-clusters. Accordingly, a metal–imido intermediate generated by stepwise deoxygenation of the nitro group on the cluster core was maintained in the reaction scheme (see Scheme 8). However, in order to rationalize the drastic influence of alcohol on the activity of this catalyst, the carbamate does not simply result from the trapping of the isocyanate by alcohol.



Scheme 8.

In fact, alcohol was proposed to intervene in an earlier step to form an alkoxycarbonyl ligand which could then subsequently be coupled with an amido ligand from a neighboring metal center by a two-center reductive elimination process. The amido ligand results from protonation of the imido intermediate [199]. This mechanism resembles these previously proposed for oxidative carbonylation of amines [15,35,47,66]. Such a mechanism will also be invoked later in the indirect carbonylation of nitrobenzene using formic ester in the place of alcohol [80]. As supporting evidence for the intermediacy of a metal–imido complex, they reported that a pre-synthesized mono-imido cluster can be used as catalyst precursor with quite the same efficiency as the usual $Ru_3(CO)_{12}$ cluster. However, attempts to model the carbonylation step under milder conditions with this imido cluster in stoichiometric reactions were not conclusive [121]. The nuclearity of the active species in such systems is a matter of concern, since such clusters are in equilibrium with mononuclear species under the conditions of the transformation [177,236,237]. Accordingly, Cenini et al. were cautious about this point and pointed out that monomeric intermediates generated from $Ru(CO)_5$ could account for the catalysis as well [121], especially since they had demonstrated that the latter could also catalyze the transformation efficiently [199]. More recently, the simultaneous occurrence of two catalytic pathways involving low nuclearity and high nuclearity aggregates was proposed for a closely related reaction [234].

The pronounced promoting role stated for the ammonium chloride co-catalyst was ascribed to the chloride anion. In the initial mechanistic proposal, formation of a chlorocarbonyl functionality on the cluster core that would easily be transformed in an alkoxycarbonyl ligand in subsequent steps had been tentatively proposed (see Scheme 8). Later, Geoffroy proposed an alternative explanation where halogenide ions assist the insertion of carbon monoxide in the metal–nitrogen bond of the coordinated imido ligand (see Scheme 9) [238–240].



Scheme 9.

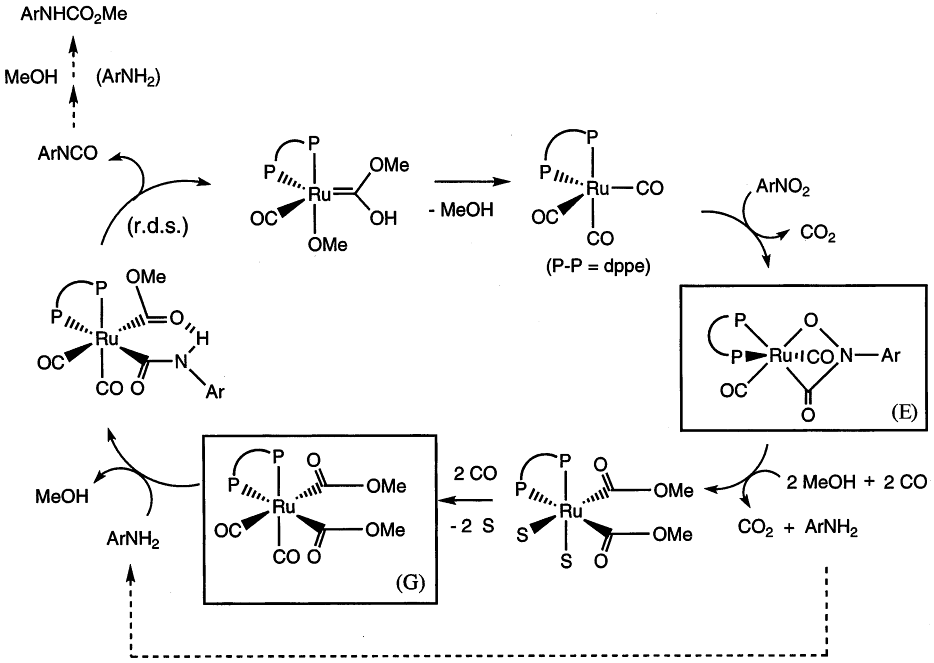
A more detailed study of this particular promoting effect was published later after systematic reactivity studies on ruthenium and osmium model clusters [241–243]. In line with these studies, the formation of $[XRu_3(CO)_{11}]^-$ from a $Ru_3(CO)_{12}$ precursor was also investigated more recently [244,245]. Such a promoting mechanism is, however, not general to all cluster-based catalysts. For instance, it appears not to be effective with iron clusters [246]. Additionally, even with $Ru_3(CO)_{12}$, it only partly explains the role of the ammonium chloride salt, since it was established recently that the nature of the cation also plays an important role in the promoting process [247]. A cooperative mechanism where the oxygen atom of the carbonyl ligand activated by chloride is simultaneously coordinated by the cation of the salt has been suggested.

With polynuclear carbonyl clusters such as $Ru_3(CO)_{12}$ or $Rh_6(CO)_{16}$, addition of a neutral chelating ligand like 1,2-bis(diphenylphosphino)ethane (dppe) or phenanthroline (phen) proved to increase notably the conversion and the selectivity of the catalyst for indirect carbonylation, and does so even in the absence of tetrabutylammonium chloride. This effect was much less pronounced when non-chelating ligands such as triphenylphosphine were used. Since good ligands that could break down the polynuclear structure of the precursor and stabilize mononuclear intermediates constituted the best co-catalysts for these systems, it was believed that low nuclearity complexes were the active species[6] [102,248,249]. Again, and curiously, when used in the absence of alcohol (i.e. direct carbonylation conditions) these catalytic systems were far less active for isocyanate formation (Tables 1 and 2) [102,145].

3.2.2. The (dppe)Ru(CO)$_3$ and related catalysts

In 1989, a study of the indirect carbonylation of nitrobenzene catalyzed by (dppe)Ru(CO)$_3$ was initiated by Gladfelter et al. [120,202–206,250] This resulted in the discovery of an original mechanism involving mononuclear complexes (see Scheme 10). Various intermediates like (E) and (F) were isolated and structurally characterized, whereas most of the others where spectroscopically observed by high pressure FT-IR.

The catalytical transformation involves a mono-deoxygenation of the nitroaromatic to give a four-membered metallacycle incorporating the nitrosoaromatic (E).



Scheme 10.

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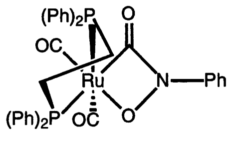
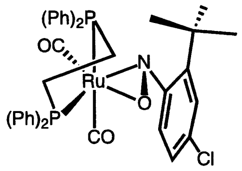
[6] In independent studies [248,249] Mestroni et al. have shown that the added ligand causes a decrease of the nuclearity of the active species in related catalytic transformations with similar precursors.

Regarding the nitroaromatic activation process, in situ EPR data are consistent with monoelectronic electron transfer from metal toward the nitroaromatic to give a radical ion pair [202,203]. The existence of a complexed nitrosoaromatic intermediate has been established by isolation and structural characterization (F) [206,250]. Further, kinetic and thermodynamic data obtained in a recent investigation support an inner sphere electron transfer step, occurring within a donor–acceptor complex between the Ru(0) catalyst and the nitroaromatic substrate [250]. The metallacycle (E) is subsequently opened by nucleophilic attack of the alcohol to form aniline and the corresponding alkoxy complex, the latter giving a bis-alkoxycarbonyl intermediate which is then converted back into the initial species of the cycle by external attack of the aniline via a transient hydroxy–methoxy carbene species.



(E)



(F)

This is proposed to be the r.d.s. of the process [205]. The kinetics of the process could be determined by GC-analysis of samples withdrawn from the reactor. The experimental rate law (Eq. (12)) exhibited first order dependence in catalyst concentration and amine, and also inverse dependence in carbon monoxide [120]. The activation energy could be determined for both aniline (31 ± 6 kcal mol^{-1}) and carbamate formation (19 ± 3 kcal mol^{-1}). A stoichiometric investigation of the carbamate forming step (r.d.s.) could be performed by reacting the resting state (G, Scheme 10) of the catalyst with aniline. This confirmed the previous results and a more precise understanding of the final steps of the cycle could be gained [205].

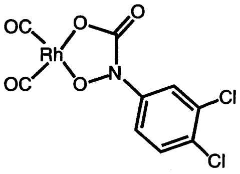
$$d[ArNO_2]/dt = k_1[Ru]/P_{CO} + k_2[Ru][ArNH_2] \qquad (12)$$

With this elegant work, good experimental insight could be gained on most of the steps and especially on the nitroaromatic activation process, giving strong support to the proposed mechanism. Importantly, the intermediacy of aniline, traditionally considered as a byproduct in nitrobenzene carbonylation, was established in this process. Compared with the previous proposal (see Scheme 8) the catalytic cycle becomes now quite intricate, since urea would be the primary product of the catalysis formed by generation of aniline in the reaction medium. Conceptually, the reaction mechanism can be subdivided in two parts; (i) a reduction of the nitroaromatic in the corresponding amine, and (ii) an oxidative carbonylation of the amine to give urea (the oxidant in this process being the nitro substrate), subsequently alcoholized into the carbamate and constituting the main product isolated.

Finally and importantly, this work suggests that a similar mechanism may be operative starting from different mono- or polynuclear ruthenium precursors when ad hoc chelating ligands are present. Indeed, a similar law was found starting from $Ru_3(CO)_{12}$ and dppe [120]. This observation is very important regarding the large promoting effect stated when some chelating ligands were added to $Ru_3(CO)_{12}$-containing catalytic systems and gives further credence to the belief that low nuclearity intermediates are the actual active species in most of these cluster-based systems. An analogous rate dependence on catalyst and carbon monoxide concentrations has also been found for a ruthenium catalyst activated by chelating ligands [181]. Thus, similar chemistry may be operative with other ruthenium-based catalysts, although the nuclearity of the active species in its resting state may depend on the type of chelating ligand used. For instance, when the dppe ligand was substituted for the dppm ligand in Gladfelter's system, dinuclear intermediates never observed with the former ligand were formed [251]. The intermediacy of a nitroso complex was also proposed in the case of the mononuclear $[Ru(saloph)Cl_2]^-$ complex by UV spectroscopy [180,252]. The activation energy for this catalyst incorporated in a tetradentate ligand is, however, much higher (38 kcal mol^{-1} at 160°C), with $\Delta H^{\neq} = 37.0$ kcal mol^{-1} and $\Delta S^{\neq} = 86.0$ eu [252].

3.2.3. The ([PPN][Rh(CO)$_4$]/phen) system

In 1994, a quite similar catalytic cycle was advanced for the $(PPN)[Rh(CO)_4]$/phen system by Ragaini et al. [102,112,253]. A study involving heterogeneous catalyst precursors indicated that the transformation was effected by homogeneous species [156].

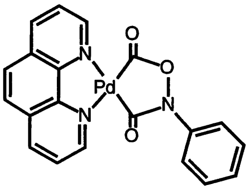


(H)

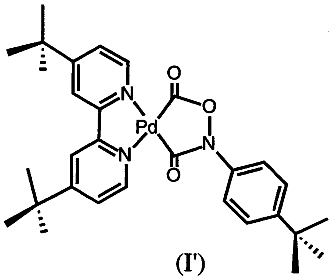
Regarding the nitroaromatic activation step, an outer sphere monoelectronic transfer was proposed to initiate the transformation based on in situ ESR studies which allowed detection of free nitro radical anions. A subsequent independent study with similar complexes gave further support to the initial electron-transfer hypothesis, but radical-ion pairs were identified in solution this time [254]. As was noted quite recently [56], these radical ion pairs are perhaps not relevant from the actual catalytic cycle, since they were generated with stoichiometric nitroaromatic amounts. Amine intermediacy is proposed based on the fact that aniline could be oxidatively carbonylated by the system in the presence of a nitroaromatic substrate, acting as the oxidant. Isolation and structural characterization of a metallacyclic mononuclear species was also possible (H). This complex is a structural isomer of the proposed five-membered intermediate (I) proposed with the ([Pd]/phen/H^+) system (see Section 3.2.4). The complex (H) is also believed to be an intermediate. Stoichiometric reactivity studies indicate that (H) can generate an 'imido' moiety under the reaction conditions, the latter being trapped with nitrosobenzene. Here again, these results cast some doubt about the polynuclear nature of the intermediates in cluster-based systems. A contrario to what could be expected [102,248,249], (H) does not react with good ligands like phenanthroline and is still quantitatively formed in their presence. Thus, the promoting role stated for diimine ligands with rhodium cluster-type catalysts does not appear to only originate from their chelating ability. While involvement of the diimine in the catalytic process is clear from the very decreased efficiency of the system when the ligand is omitted [182], another explanation for the beneficial role of these ligands was proposed recently with iron-based systems [255]. In these systems, the chelating ligand appears to promote the otherwise slow reduction step of the polynuclear precursor.

3.2.4. ([Pd]/N–N/H$^+$) systems

Similar palladium-based systems made from a diimine ligand and a homogeneous or heterogeneous metal precursor in the presence of a Brönsted acid promoter were independently investigated by many groups [90,91,100,109,187–191,194,210,216]. Some common trends have been delineated. First, regardless of the precursor used, the whole transformation appears to happen homogeneously [100]. At the end of the catalysis, even when using an heterogeneous precursor[7], similar metal complexes containing the diimine ligand could be detected in solution by UV–vis spectroscopy[8] [194]. However, mononuclear intermediates are favored in the proposed mechanisms, the nature of the intermediates in this process is still speculative. Indeed, while diimine ligands were known to stabilize low-nuclearity complexes, it has recently been demonstrated that they could stabilize 'giant clusters' or colloids as well, especially with palladium [257,258]. The mechanism was initially believed to proceed by intermediate isocyanate formation by a mechanism quite similar to the one proposed for $(Py)_2PdCl_2$ (see Scheme 5), followed by rapid alcoholysis of the isocyanate formed [190]. Later on, Leconte et al. managed to isolate the complex (I) from reaction medium under milder conditions than the catalytical ones and the analog (I′) could be structurally characterized by Osborn et al. [259]. Very recently the authentic palladacycle (I) could also be independently characterized structurally [260,261].



(I)



(I′)

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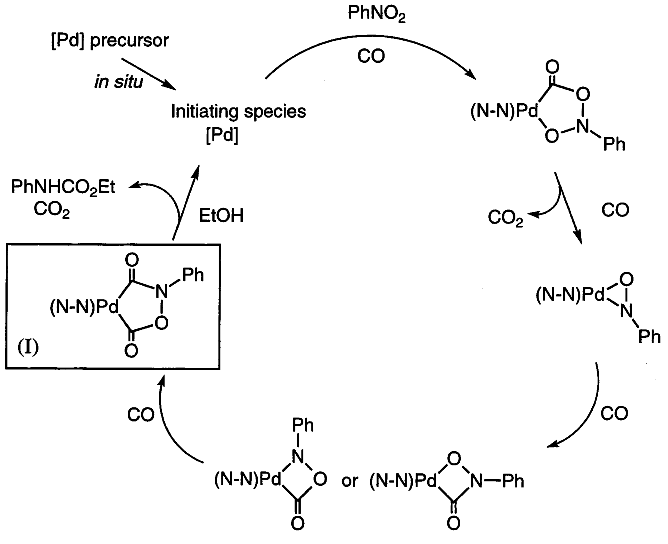
[7] Independent studies also established that the diimine ligands were able to extract metal atoms from bulk metals [43,100,190,194,210,256]. This can help to understand why many attempts to heterogeneize bipy-containing homogeneous systems by depositing/adsorbing them on various supports proved to be disappointing [39,43,156,196]. One of these attempts though, was apparently more successful [191].

[8] Mestroni showed notably that the nature of the support had very little influence when heterogeneous catalyst precursors were used, whereas an acid cocatalyst and a ligand were needed for activity [156,194].

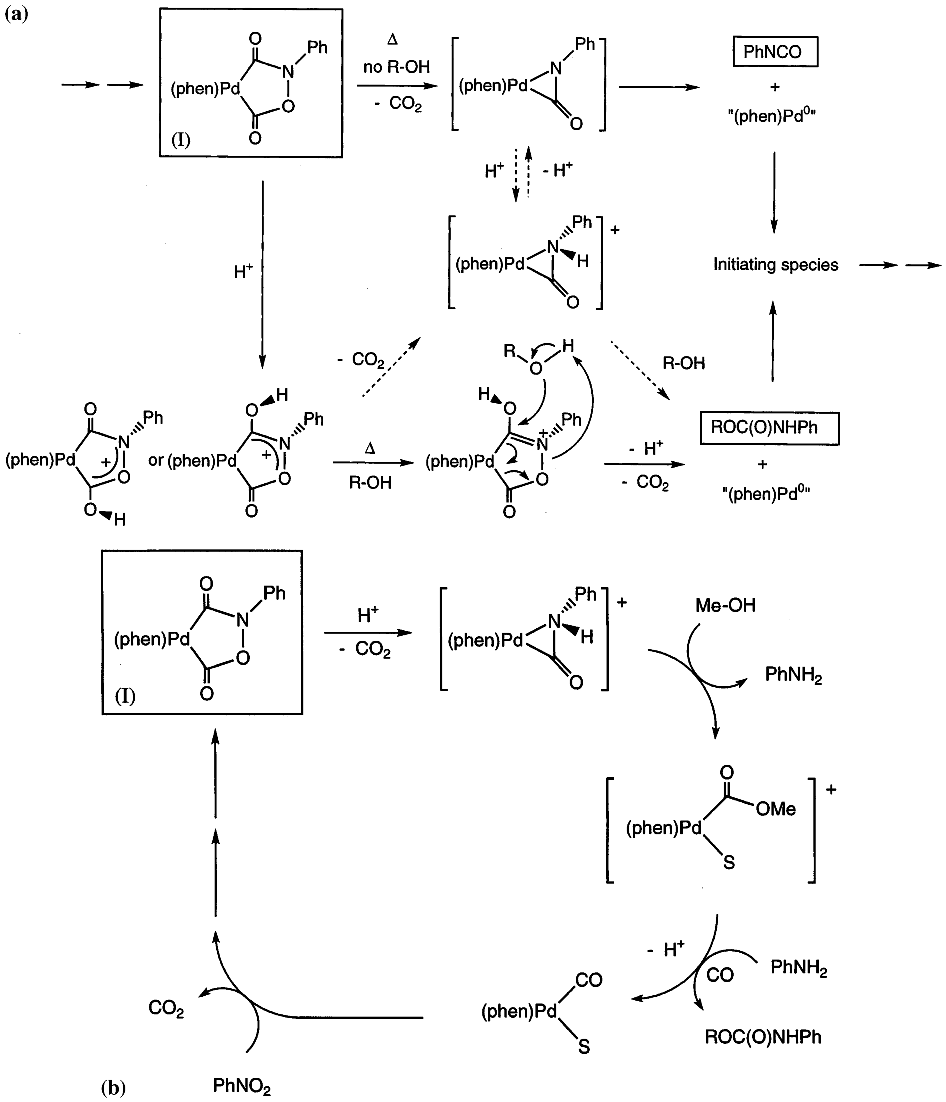


Scheme 11.

The ring-opening reactions of this metallacycle (I) in the presence of alcohols and various Lewis acid promoters, suggested that it was an intermediate in the catalytical cycle [216]. Thus, a mechanism based on metallacyclic intermediates (Scheme 11), resembling the one proposed by Schwetlick for the direct transformation (Scheme 4) appears likely.

In this mechanism, no metal–imido intermediate is formed and the carbamate is generated by proton catalyzed alcoholysis of (I) (see Scheme 12). Easy decarboxylation of five-membered metallacycles possessing a CO_2 moiety similarly coordinated has precedence in the literature [262,263]. The decisive role played by the nature of the Lewis acid on the distribution of the organic products formed was at the origin of such a proposal. This ring-opening step is believed to be rate-determining for the catalysis, but no precise kinetics could be established starting from (I) due to the poor solubility of the compound under mild conditions. Global kinetic studies were in accordance with such a scheme and indicated notably a first order dependence on Pd-catalyst concentration, a zero order relative to nitro substrate and no induction period at 140°C under 60 bar of carbon monoxide in the presence of acid co-catalyst when complex (I) was used as precursor [119].

After protonation of (I), the formation of the carbamate may take place, either by a concerted alcoholysis ring-opening mechanism, either by the intermediacy of a π-ligated isocyanate complex (see Scheme 12(a)), depending on the rate of the decarboxylation step relative to the nucleophilic attack of the alcohol. During stoichiometric alcoholysis reactions of (I), protons favor the formation of carbamate while Lewis acids like $FeCl_3$ were demonstrated to favor nitrosobenzene formation and derived products, possibly by other ring-opening processes [119,264].



Scheme 12.

This is in accordance with the large promoting role stated for carboxylic acids relative to Lewis acid promoters (see Table 2) [187]. The presence of a non-coordinating associate base is also essential for the activity of the systems, but a clear relationship to its pK_a could not be proven [91,189]. The promoting effect of the anion was related to the need to generate in situ a palladium(II) species with labile ligands for initiating the catalytic cycle [100,188,190]. Another promoting effect was reported for traces of chloride ions [190], but this effect was contested and has still no clear explanation for now [100], although formation of anionic chloro zerovalent complexes during the induction period has tentatively been proposed [58].

Compared with other mechanisms previously proposed for indirect systems, such a mechanism minimizes the influence of the alcohol on carbamate formation and is consistent with the fact that this system retains its activity for isocyanate production in the absence of alcohol, under quite similar conditions [156]. Moreover, a significant difference with previous systems is the fact that protons are present in excess here and will disfavor the formation of palladium(II) carbamoyl or alkoxycarbonyl complexes [265–268]. An alternative mechanism, closer to the one previously proposed for the ruthenium and rhodium catalysts (see Scheme 12(b)) was nevertheless advanced recently for this system [90,91,100], but experimental evidence supporting it is currently subject to debate [58].

Interestingly, this system has also been studied when the Brönsted acid is replaced by $CuCl_2$ [187]. The kinetics of the global process are apparently first order in carbon monoxide, in nitroaromatic and in catalyst concentration. In this case the r.d.s. of the global process must be different. The average thermodynamic activation parameters found were $E_a = 30.0$ kcal mol^{-1}, $\Delta H^{\neq} = 26.06$ kcal mol^{-1}, $\Delta S^{\neq} = 112$ eu and $\Delta G^{\neq} = 16.52$ kcal mol^{-1}. According to these endothermic parameters, an r.d.s. corresponding to the first deoxygenation step of the nitroso group in a classical mechanism based on an imido intermediate has been put forward.

These kinetic parameters are also very different from these reported with heteropolyanion derived catalyst ($PdCl_2$/HPA) systems [158]. First order dependence of the rate versus carbon monoxide and catalyst concentration was stated ($E_a = 38$ kJ mol^{-1}). For this system an apparent fractional order dependence (0.43) versus the nitroaromatic was also found, but no mechanism was proposed. Independent studies revealed that the mechanism might proceed by intermediate formation of aniline and a change of the r.d.s. depending on the nitroaromatic substrate concentration was proposed to explain the fractional order observed [214].

4. Discussion of the mechanisms

Somewhat artificially, we have still kept the discussion regarding direct and indirect carbonylation mechanisms separated in the following section, although insight into any of these transformations has helped in understanding the other. Data pertaining to both reactions will be discussed first.

4.1. General questions regarding nitroaromatic carbonylation reactions

4.1.1. The nuclearity of the intermediates

For both direct and indirect carbonylation reactions, the nature (homogeneous or heterogeneous) and the nuclearity of the catalytical system are difficult matters. These transformations were usually considered to be achieved in homogeneous phase regardless of the exact mechanism, since the reaction mixtures were usually homogeneous [63,156]. In cases where this is not true, the separation line between heterogeneous and homogeneous catalysis is difficult to draw [58,62,98]. An illustrative example is given by Braunstein et al. for the direct carbonylation: an heterogeneous precursor generated by deposition of a mixed palladium–molybdenum cluster on alumina gave essentially the same results as an equivalent mixture of homogeneous precursors[9] [153]. For indirect carbonylation as well, the heterogeneous nature of the medium is often not significant, and although, efficient heterogeneous catalysts have been claimed (see Table 2), nothing was usually said about their deactivation upon repeated use [41,44,182,186]. Many of the ligands used in these transformations have proven able to extract metal atoms from bulk materials (see footnote 7), and a homogeneous catalyst could easily be generated from the heterogeneous precursor [156,165,185]. Thus, the existence of heterogeneous mechanisms for these transformations remains speculative, apart perhaps for some rare exceptions [148,182,191,269], whereas homogeneous mechanisms have clearly been identified in definite cases (see Section 3) and are usually considered as the dominant reaction pathway for most of the systems reported. Finally, the recent report [157] that 'giant clusters' [257,258] could catalyze the direct transformation to some extent also brings into question the possibility of colloidal catalysis for these transformations [270,271].

When a homogeneous mechanism is assumed, nothing general can be established from the available data regarding the nuclearity of the intermediates involved in the catalytic cycle. This is particularly true when cluster complexes are used as precursors, since these may equilibrate with mononuclear carbonyl species under the reaction conditions [272]. When used as promoters without ligands or in presence of poor ligands, the simultaneous occurrence of polynuclear and mononuclear intermediates belonging to parallel catalytic cycles has been proposed [234]. However, when chelating ligands like phen or dppe are present, strong indications were gained in favor of mononuclear species being the true catalytic intermediates in indirect carbonylation processes, regardless of the nuclearity of the catalyst precursor used. First, in situ high pressure IR measurements suggested that mononuclear complexes were dominant in solution in several instances, then, most of the complexes isolated and believed to be part of the catalytical cycle (F–I′) were mononuclear.

4.1.2. The problem of the nitro substrate activation

The question of the activation step and the first deoxygenation of the nitro substrate is also central to both direct and indirect transformations. These steps usually precede the r.d.s. They have been proposed to be rate-determining for the carbonylation process only in a few occasions [109,158,187,218]. Until recently, for all homogeneous mechanisms the nitro-activation process were very poorly understood and highly speculative [110,111]. Initial activation of the nitro functionality

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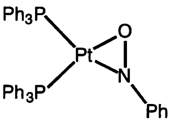
[9] Despite comparable catalytic performances, the heterogeneous MMCD catalyst precursor generated after decomposition of the cluster upon pyrolysis was mostly recovered as a precipitate at the end of the reaction, while a large part of the homogeneous mixture of precursors remained in solution. In the second case, a very small amount had also been deposited on the walls of the reaction vessel since further catalytic activity could be observed after replacement of the solution by a new load of reactants.

was believed to be induced by outer sphere electron transfer from the catalyst to the substrate giving the nitro radical anion, possibly stabilized by complexation to the metal center [273–275]. More recent results with indirect systems now give further credence to this hypothesis [112,246,254]. A quite common proposal is that the nitro radical anion formed reacts subsequently with a carbonyl complex to form a five membered metallacyclic intermediate (see Scheme 13). Decarboxylation would then give a nitrosoaromatic complex that can react further by carbon monoxide insertion [273].

In this sequence, many experimental facts argue in favor of the intermediacy of a nitroso complex. (i) First, nitroso complexes have often been isolated after reduction of nitroaromatics by carbonyl complexes [276,277], and sometimes in reaction conditions very close to the catalysis (like F) [154,206,250,278]. (ii) Secondly, it has been shown in many instances that nitrosoaromatics, when used as substrates in reductive carbonylations, were often able to generate the same final organic products as the nitroaromatic did [154,181,279–283]. In some cases, however, the selectivity for the different products isolated varied [90]. (iii) Then, it has been stated that nitrosoaromatics complexes, when put under carbon monoxide pressure, will either decompose and generate typical organic products of the catalysis [181,279,284–287], or form stable metallacycles having structures close to those postulated for certain intermediates (like $\boldsymbol{i_4}$) [119,203,253,288]. In these reactions, the applied pressure and the nature of the reaction medium have a strong effect on the nature of the products formed [238,280,286,287]. (iv) Finally, with polynuclear carbonyl complexes, nitrosoaromatics behave like nitroaromatic substrates; they can lead to the formation of metal–imido complexes in stoichiometric or catalytic reactions [229,238,240,243,246,289–293].

Regarding the structure of this nitroso intermediate $\boldsymbol{i}_3$, a side-on π-ligated mononuclear structure such as (F) appears likely[10]. Notably, ab initio calculations carried out on the mononuclear platinum complex (J) indicate that the π-ligated side-on mode is more stable than the *N*-σ-ligated mode [297].



(J)

Very strong support for the sequence depicted in Scheme 13 was brought forward recently in the work of Gladfelter et al. with the (dppe)Ru$(CO)_3$ [206,250]. These researchers could model the first part of the transformation i.e. the first deoxygenation to form a nitroso complex. They concluded that the initial step was indeed an inner-sphere electron transfer from the Ru(0) catalyst to the nitro substrate, in a slightly congested activated complex somewhat resembling $\boldsymbol{i_1}$. Finally, they isolated

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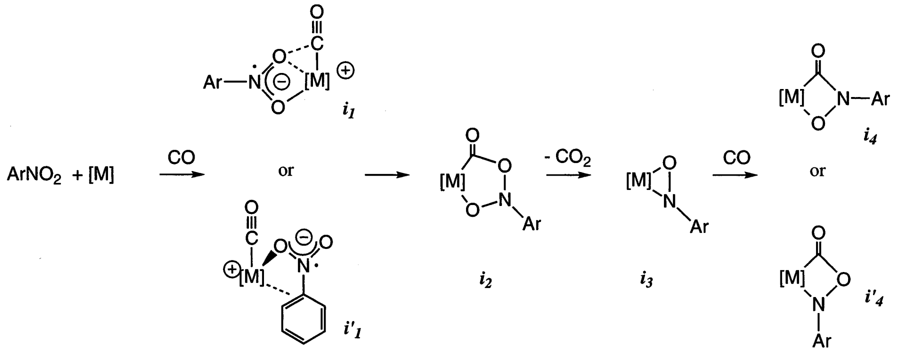
[10] Whereas *N*-σ-ligated nitroso complexes were known [294,295], the first example of a structurally characterized *O*-σ-ligated nitroso complex has been only recently reported with iron porphyrins [296].

and characterized (F) which constitutes the only structurally characterized π-ligated mononuclear nitrosoaromatic complex with Group VIII metals, apart from (J)[11].

The other activation process that had been suggested for the heterogeneous Rh-based system studied by Basset et al. and involving metal oxo intermediates (see Scheme 6) was never really questioned for homogeneous Group VIII catalysts. Such oxo ligands are only seldom encountered with late transition metal complexes [284,300,301]. To our knowledge, the only clearly identified example involving similar oxo intermediates in a related homogeneous deoxygenation process of the nitro group is reported with molybdenum [302]. While this nitro-activation pathway might indeed be operative with oxophilic metal centers [303–307], we consider it unlikely with homogeneous Group-VIII catalysts. This reaction sequence could nevertheless be operative as a side-reaction[12], when early transition metal salts are present as promoters [6,106–108,160,308].

In conclusion, the reaction sequence depicted in Scheme 13 now constitutes apparently the most sensible mechanism for the nitro-activation steps with Group VIII catalysts. Furthermore, it is quite probable that coordination of a Lewis acid to the oxygen atoms of the nitro group will significantly lower its activation energy [93,107,150].



Scheme 13.

4.1.3. *The role of the co-catalyst*

Apart from some cluster-based systems, where halide salts were used as promoters (see Section 3.2.1), the role of the co-catalyst is far from being well understood. In most of the catalytic systems studied the inorganic promoter was

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[11] Structurally characterized relevant polynuclear π-ligated nitroso complexes are, however, known with Group VIII metals [284,291,298,299].

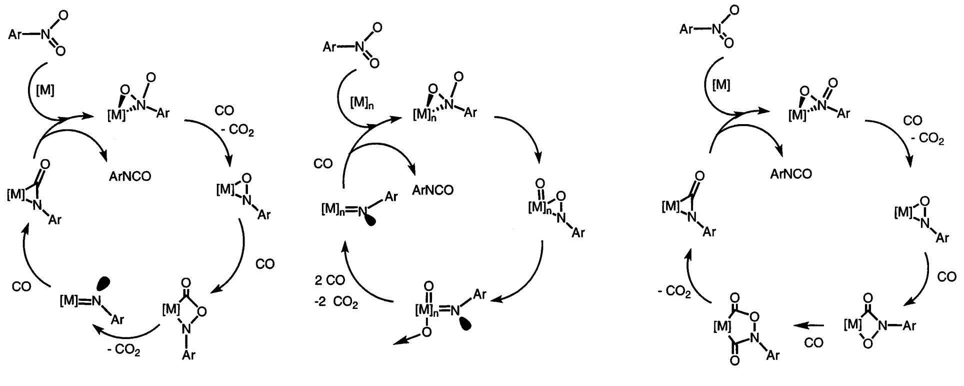
[12] It has been suggested that the Lewis acid could perform the complete de-oxygenation of the nitroaromatic and give the corresponding imido ligand. The latter would then be carbonylated on the catalyst after transmetallation [6,106–108]. This proposal appears however not to constitute the main reaction pathway, since the catalyst is often operative without any co-catalyst present. See also [219].

generally a Lewis or a Brönsted acid. Depending on the system used, very different suggestions were made to explain its promoting effect. Noticeable examples are: (i) to help activation of the nitro function toward reduction by coordination to the oxygen (see footnote 12) [91,93,107,150,269,308,309], (ii) to influence the evolution of metallacyclic intermediates by coordination [216,218b], (iii) to help recycle eventual inactive (heterogeneous or reduced) species by oxidation [58,97,109,119,160,174,186,211,212,220], (iv) to favor carbon monoxide insertions [193,247,269], or (v) to trap side-products detrimental to the catalysis [109,155]. Additionally for Brönsted-type co-catalysts, another role could also be to inhibit the competitive carbonylation of the alcohol into oxalic esters [265,266]. Indeed, it has been demonstrated in several instances that protons disfavor the formation of palladium(II) bis-alkoxycarbonyl complexes which appear to constitute crucial intermediates in the synthesis of oxalic esters [267,268]. Clearly, the promoting role of a given co-catalyst may be multiple and will strongly depend on the nature of the catalytic system used.

4.2. *Mechanisms for direct carbonylation*

4.2.1. *The metal–imido mechanisms*

With Group VIII transition metal catalysts (see Scheme 14), two main 'types' of mechanisms have so far been proposed, depending on the formation of a metal–imido intermediate or not (type I or II). Up to the mid-1980s, the formation of a metal–imido intermediate was usually assumed in most of the mechanisms. [6,63,93,104,106,107,150,160,217,224,269,310]. As mentioned earlier, this belief finds its origin in the seminal work of Weigert [149]. The intermediacy of an imido species does in fact rationalize the formation most of the minor typical side-products isolated after carbonylation reactions (see Scheme 3). Additionally, several other experimental facts are in accordance with this hypothesis:



TYPE Ia TYPE Ib TYPE II

Scheme 14.

1. First, it has been stated very early that with typical catalytic systems for nitroaromatic reductive carbonylation, the catalyzed carbonylation of potential nitrene or metal–imido precursors like azides or azobenzenes usually produces the corresponding isocyanates or carbamates, when alcohol is present [311–313] (see Scheme 3). In the case of azides, the carbonylation can also take place without catalyst [314], but then the reaction is very unselective and sluggish [315–322]. In the case of azo compounds however, a transition metal catalyst is always needed [104–108]. Clearly, azobenzenes are not reaction intermediates in the carbonylation reaction and transient metal–imido intermediates were always invoked [105,107,108].
2. Secondly, the formation of transient imido compounds under typical catalytic conditions can indirectly be detected in the case of particular functional nitro substrates. With the usual iron [323,324], ruthenium [234,247,290,323,325–329], rhodium [323,330], palladium [325,331–338] or platinum [339] catalysts, *N*-heterocyclic products containing a fragment potentially derived from the corresponding nitrene or imido intermediate in their structures were isolated as the main products at the end of the carbonylation reaction[13]. Further evidence for the formation of such species via an imido intermediate could be gained by deuterium labeling using palladium catalysts [335]. These statements and other observations [341] are all strongly indicative of the formation of a nitrene or metal–imido species during the transformation [177,217,342,343].
3. Then, most of the catalytic systems effective for oxidative carbonylation of nitroaromatics can also be used for their reduction in the corresponding anilines when molecular hydrogen[14] or water[15] are present. In these reductions, metal–imido are also likely intermediates. Such imido complexes that are easily hydrogenated or protonated would constitute the common denominator with reductive cabonylation reactions [233,355].
4. Finally, assuming the occurrence of an imido complex as an active intermediate in the process (type I), the formation of the isocyanate should occur by carbonylation of the imido functionality and release of isocyanate. In several instances, this last step could be successfully modeled in stoichiometric reactions, starting from polymetallic [355–357] or monometallic imido complexes [358–360]. While the cluster-stabilized tri-ligated imido moieties usually proved quite unreactive, resulting in no [121,238,240] or sluggish carbonylation reactions under forcing conditions [144,239,241,311], the monometallic imido complexes reacted much more readily. Carboxylation of such species can also occur in solution. Unfortunately, for now, only scant general information on the

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[13] For a caveat, see [340].

[14] For representative examples with Ru, Rh, Ir clusters see [236,344], respectively or with mononuclear Ru, Rh and Pd complexes, see [111,345,346].

[15] For representative examples with Ru, Rh clusters see [122,347–350], respectively, or with mononuclear Ru, Rh, Pd and Pt complexes see [115,351–354].

reactivity of mononuclear imido complexes of the Group VIII metals is available [358–363]. These compounds appear to be very sensitive to the presence of protons, and readily form the corresponding amine [116,117,362].

4.2.2. The metallacyclic mechanism

Despite all these experimental facts rendering a transient metal–imido species in the medium a likely source for many products of the carbonylation reaction, its role as an actual intermediate in the catalytic transformation of simple nitroaromatic substrates has never been proven. Accordingly, a type-II mechanism (involving no such intermediate) could also be operative for the formation of isocyanate[16]. Such a mechanism, although evoked very early by Schwetlick et al. (see Section 3.1.1), has gained more consideration recently from investigations conducted on the ([Pd]/phen/H^+) system (see Section 3.2.4). Supporting facts for it can be listed as follows:

1. Several metallacycles like (I) have been isolated with palladium catalysts under milder conditions than the catalytic ones in the presence of alcohol [259–261]. These species were characterized crystallographically and proved to behave as intermediates in the transformation. They are exactly the intermediates that would be formed in a type-II mechanism.
2. General evidence for the occurrence of such intermediates with other catalysts comes from ab initio theoretical calculations performed on the side-on π-ligated nitroso previously mentioned platinum complex (J). These calculations indicate a larger electronic density on nitrogen in this type of complex and thus preferential carbon monoxide insertion in the [M]–N bond to form a four-membered metallacycle analogous to $\boldsymbol{i_4}$ in Scheme 13 [297]. Favored insertion into the M–N bond rather than into the M–O bond in (J) could also be experimentally confirmed by its stoichiometric reactions with various electrophilic cumulenes independently synthesized [285,364,365]. In line with these results, the complex (E) which was isolated with a ruthenium catalyst under indirect carbonylation conditions has been characterized crystallographically. It is similar to the intermediate $\boldsymbol{i_4}$ and its involvement in the catalytic cycle has been established kinetically [206,250]. Metal–imido intermediate generation from such a species by carbon dioxide extrusion is impossible to achieve without rearrangement. Thus, the formation of an imido-intermediate from a nitroso-intermediate in the presence of carbon monoxide, as postulated in a type Ia mechanism (via $\boldsymbol{i'_4}$), appear to be disfavored relative to the formation of the corresponding five-membered metallacyclic intermediate (like I) generated by carbonylation in a type II mechanism (see Scheme 14).
3. The reactivity of four- or five-membered hetero-metallacycles structurally close to some of the intermediates postulated in mechanisms of type-II, gives credence to this proposal. Typically, it has been shown that metallacycle extension by incorporation of carbon monoxide or contraction by loss of carbon dioxide is

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[16] In this case, an imido-complex could also be generated in the medium by a parallel minor pathway and account for the side-products isolated.

an easy process [366]. Moreover, related metallacycles have often been isolated from the reaction medium after reaction of nitroaromatic carbonylation without alcohol, indicating that such species can easily be generated under typical carbonylation conditions [253,288].

4.3. Mechanisms for indirect carbonylation

4.3.1. The role of alcohol; relation to direct carbonylation mechanisms

The indirect carbonylation reaction was initially believed to proceed by a similar mechanism to the direct one, followed by a trapping reaction of the isocyanate by the alcohol as sketched in Eq. (1) and Eq. (3)[17]. In the early 1970s, such a belief was also supported by the demonstration that the 'trapping' reaction (Eq. (3)), known for a long time with free isocyanates (see Section 2.1.2), was operative as well with isocyanates complexed on various metal centers [125,126]. Around the mid-1980s however, more and more experimental facts accumulated that were suggestive of more intimate mechanistic differences between the direct and indirect carbonylation reactions. For instance, it was discovered that the presence of alcohol often had a strong influence on the activity of a given system when compared with the corresponding direct process [121,367,368]. Moreover, the reported influence of temperature using the same catalysts, in the presence or not of alcohol, was often not likely to be compatible with the hypothesis of a common carbonylation mechanism for both processes [233]. Finally, it was reported in many instances that the nature of the alcohol itself was determining regarding the yield in carbamate [121]. In some cases, depending on the catalyst used, alcohols possessing easily activated α-hydrogens constituted a molecular hydrogen source in the medium and led mainly to the formation of aniline or other hydrogenated products compared with more conventional alcohols used in these processes [235,369]. All these facts suggested that the alcohol interacts with the catalyst during the carbonylation process and does not simply trap the isocyanate primary produced by the catalysis. Accordingly, the attempted use of some very efficient systems for carbamate formation in the absence of alcohol often resulted in no or very low turnovers in isocyanate [67,101]. Conversely, some typical systems for direct carbonylation proved much more active for carbamate generation when alcohol was present [156], while some others were completely inactive [37,181,182]. Considerations regarding the sensitivity of the active species toward protic impurities were sometimes invoked to rationalize these discrepancies [67,101], but eventually, mechanisms where alcohol took part in the genesis of the active species were considered (see Scheme 15). For instance in (III) and (IV) alcohol intervenes very early in the catalytic cycle and its is essential for the carbonylation/deoxygenation of the substrate to proceed efficiently [67,101,121,177]. Among the mechanism proposed, only (V) remains somewhat connected to the simple scheme mentioned earlier and invoking isocyanate as the primary product of the catalysis, subsequently trapped by alcohol.

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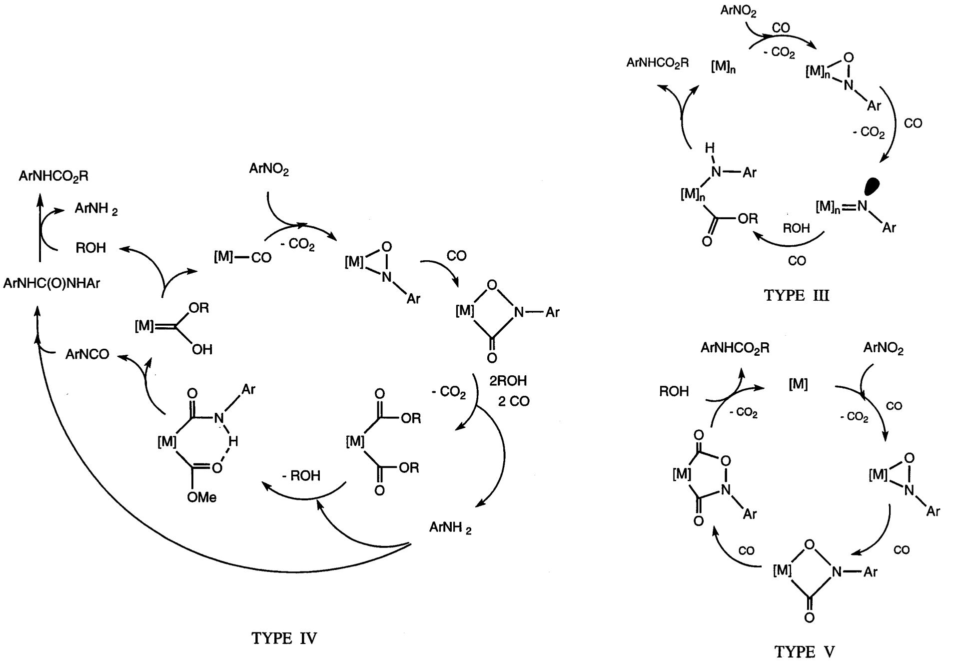
[17] While such a proposal is still advanced as a working hypothesis, it often does not rest on thorough mechanistic investigations [252].



TYPE IV

TYPE III

TYPE V

Scheme 15.

4.3.2. *The different indirect mechanisms and their experimental basis*

All these mechanisms (III–V) for indirect carbonylation were proposed for presumed homogenous catalysts. Only recently were some mechanisms put forward with heterogeneous intermediates. Most often, these consisted in heterogeneized catalysts composed of complexes immobilized on various supports[18] [182,191]. Thus, the tentative mechanisms proposed were very similar to the homogeneous mechanisms and involved molecular intermediates.

In the homogeneous mechanisms (III–V) the initial steps (nitro activation and first deoxygenation) are believed to be similar to those delineated for direct carbonylation (I–II). None of them, however, presents a step where a metal–imido intermediate is generated and carbonylated into the isocyanate (type Ia). Since early studies on imido complexes, the carbonylation of such an intermediate relative to its competitive protonation to give an amido species was questionable when a proton donor like alcohol was present [116,117,362,370]. In this respect, the mechanism (III), initially advanced for ($Ru_3(CO)_{12}$/TBACl) and other cluster-based systems, was the first serious proposal for indirect carbonylation, despite presenting very little experimental support. Now, (IV), clearly established for (dppe)$Ru(CO)_3$, appears to be the mechanism operative with $Ru_3(CO)_{12}$ in the presence of dppe, and

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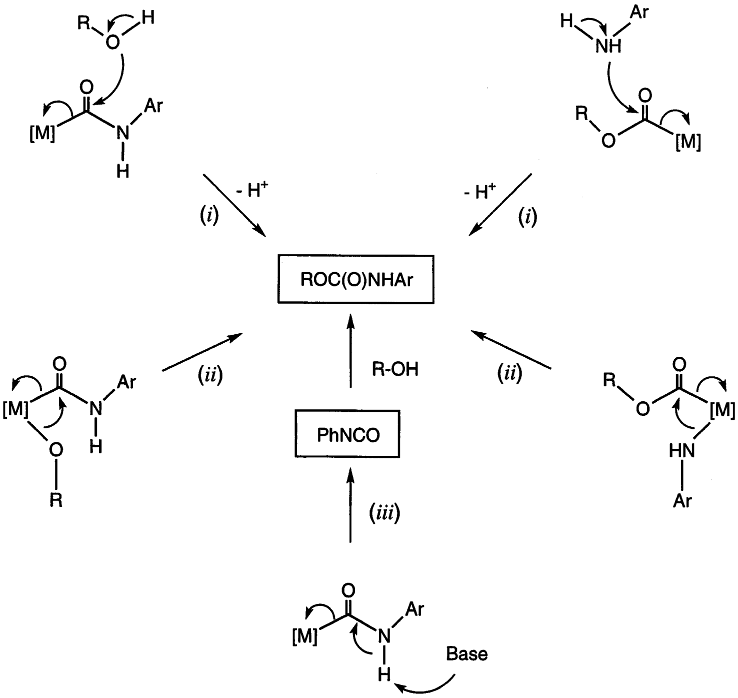
[18] See also Refs. [41,44].



Scheme 16.

possibly also with other cluster-based systems for which (III) had formerly been proposed. This mechanism finds indubitably the strongest experimental support among these proposed (III–V). Remarkably, (V), which has been proposed for the ([Pd]/phen/H^+) system, is the only mechanism that allow a catalyst to retains its activity for isocyanate production when alcohol is absent. Indeed, no free isocyanate can possibly be generated by (III) or (IV) under direct conditions. A Brönsted acid promoter was present in most catalytic systems for which mechanism (V) has been put forward. In that respect, the absence of carbamoyle or alkoxycarbonyl intermediates in (V) is consistent with the presence of protons, which are known to disfavor the formation of such complexes [265–268].

Now, if one wants to tie together all mechanistic data available for indirect carbonylation reactions on Group VIII catalysts, currently, no unifying picture emerges and, depending on the nature of the catalytic system used, either (IV) or (V) appear very likely to be operative.

4.3.3. The question of aniline intermediacy

Oxidative carbonylation of amines (see Scheme 2; path *f*) is a transformation catalyzed by very similar catalytic systems, despite usually occurring under more oxidizing conditions[19]. While its mechanism has not been clarified up to now [59], several studies have delineated possible pathways for the carbamate generation steps (see Scheme 16). These are (i) external nucleophilic attack of one of the substrates (respectively, alcohol or amine) on the carbonylated form of the other (respectively, carbamoyle [36,38] or alkoxycarbonyl [371]) present as a ligand on the metal center, (ii) direct reductive elimination of the carbamate, the constituting parts being present as ligands on the catalyst, such as for instance the amido and the alkoxycarbonyl moieties in (III) [37,43,45] or (iii) deprotonation of a carbamoyle ligand to generate the free isocyanate (readily converted into carbamates by the alcohol) along with the reduced metal center. In this case, unless a co-catalyst is present[20], a basic medium was always required to effect the deprotonation [375,376].

In (III) and (IV), the carbamate is formed by pathways (respectively, reductive–elimination or intramolecular ligand rearrangement) reminiscent of mechanisms proposed for these amine oxidative carbonylation processes [15,35,47,50,66]. The oxidative carbonylation of amine does in fact clearly take place in (IV), after aniline formation, with the nitro substrate constituting the oxidant required by the reaction (see Section 4.3.3). Such a feature does not appear explicitly in (V), but amine intermediacy has been proposed to occur subsequent to the formation of the five-centered intermediate (I) (see Scheme 12(b)). As mentioned earlier, the acidity of the medium may have a strong influence on these steps, especially those involving deprotonation of carbamoyle intermediates.

The intermediacy of aniline in this transformation was clearly established only for the (dppe)Ru$(CO)_3$ catalyst and rests mostly on the observation of an increased activity for carbamate formation in the presence of small amounts of added aniline, supported by kinetics measurements. Now, similar promoting effects induced by aniline have been reported for other indirect systems like $Ru_3(CO)_{12}$ [178,377], ([Rh]/phen) [112], ([Pd]/phen/H^+) [91] or ([Pd]/Cl^-/HPA) [214] and are also taken as an indirect evidence for aniline intermediacy [91,112,214]. In the case of palladium-derived systems, such a feature would be consistent with independent results on the formation of urea in the presence of aniline (see footnote 2) or with previous reports of the metal catalyzed generation of carbamate [68,69,71,72], where transient formation of urea was stated [43,44,46,70]. However, while such a promoting effect exerted by amine appears to have some generality among indirect systems, it was also contested in specific cases [183,378], and whether its observation can be taken as the signature of mechanisms involving amine intermediacy remains

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[19] In systems reported to catalyze oxidative carbonylation of amines, a copper cocatalyst and an oxidant (in general oxygen) are required. In the case of Pd-based catalysts, this is to reoxidize the Pd(0) in Pd(II) after the reductive coupling has occurred, as in the Wacker process [45]. However, recent investigations using chemical [78] or isotopic [73,74] labeling showed that these can be effective without such an oxidant if a nitroaromatic substrate is present. Indeed, pure aniline can be carbonylated catalytically in the presence of a sole nitrobenzene as the oxidizing agent [37,39,76]. Therefore, the nitroaromatic itself, or a derived product such as the nitroso- or the azoxy-aromatic, may effect the catalyst re-oxidation [193]. The reaction mechanisms of such processes mainly forming ureas are not well understood [90].

[20] In the presence of a copper chloride, reductive elimination of carbamyl chloride, rapidly evolving in isocyanate by HCl loss has been proposed as well [372–374].

an important question. Notably, a similar promoting effect of amines has been reported for direct carbonylations where amine intermediacy can hardly come into play [106,107]. More generally, it is now highly desirable to further clarify the relationships between indirect reductive carbonylation mechanisms (starting from nitroaromatic substrates) and oxidative carbonylation ones (starting from anilines).

4.4. Conclusions

Despite the fact that these interesting reactions were discovered more than 40 years ago, a clear overall picture of the nitroaromatic carbonylation mechanisms with Group VIII catalysts is still not available. Instead, the data are suggestive of different mechanisms being operative. First, the nature of the catalyst itself appears to have a strong impact on the elementary steps in the transformation. Then, even with a given catalyst, the presence of alcohol may also determine the course taken by the reaction sequence during the carbonylation. Obviously, more work is needed to rationalize the current data. Nevertheless, the general following statements can be made. (i) The direct or indirect transformations are likely to be homogeneous ones for most of the efficient catalysts. This question is of critical importance regarding catalyst recovery which is a major problem for industrial exploitation (see Section 5.1). (ii) Mononuclear intermediates are now usually invoked in most mechanisms, but possible simultaneous occurrences of different catalytic cycles involving intermediates of different nuclearity were proposed with cluster-based systems. (iii) For both transformations, the initial steps may be similar regarding the nitroaromatic activation. This activation process is supposed to involve one-electron transfer from catalyst to the nitroaromatic substrate followed by its stepwise deoxygenation in the catalyst coordination sphere (see Scheme 13). (iv) Regarding the direct carbonylation mechanism, the crucial question of intermediacy of a metal–imido intermediate in the cycle is currently not settled. Mechanisms without such an intermediate have been proposed equally and appear more probable in protic media. Unfortunately a good knowledge of the reactivity of Group VIII mononuclear imido-complexes is currently lacking. (v) Addition of alcohol induces fundamental changes in selectivity and activity for most of the systems. Accordingly, the proposed reaction schemes are often quite different and indirect carbonylation reactions are proposed to be more closely connected to the oxidative carbonylation of amines. Notably, the question of aniline intermediacy established with certain catalysts has to be clarified regarding its generality.

5. Direct versus indirect carbonylation for isocyanate production

5.1. Industrial potential of carbonylation reactions nowadays

Twenty years ago, most of the nitroaromatic carbonylation reactions known were insufficiently productive to replace the traditional route toward isocyanates starting from amine and phosgene (see Scheme 1) in terms of investment and cost [1].

Catalyst recovery constituted a crucial problem in all these processes, especially when expensive metals like palladium were used [41]. Industrial extension of indirect carbonylation processes catalyzed by palladium [14,379] or selenium [380,381] were nevertheless seriously considered in the late 1970s. In fact, these carbonylation reactions were quite environmentally benign in comparison with the traditional phosgene-based route and the need to develop more environmentally-friendly processes revived the research on these transformations [59,200,382–384]. Eventually, in the mid 1980s, very active catalysts were patented for the indirect reductive carbonylation of nitroaromatics. However, exactly at that time, the industrial extension of a carbonylation route for carbamate production starting from the corresponding aniline was developed by an alternative approach; an oxidative carbonylation process using a heterogeneous palladium catalyst [15,143].

Yet, nitroaromatic reductive carbonylation processes are still interesting for isocyanate production. First, the nitro-to-amine reduction step currently needed prior to any amine-based process (see Scheme 1) can be avoided. Indeed, nitroaromatics constitute an easily available raw chemical for industry and are anyway the starting material for traditional amine production. Additionally, carbon monoxide or syngas also constitute quite cheap and available feedstock [59,200,382–384]. In the future, industrial processes will have to sacrifice more and more to ecology (waste reduction) and 'atom economy' considerations, regardless of their productivity [13,385]. This is especially true for specialty chemicals where the 'plus-value' on a given product does not obligatory rest on gross production [200]. At first sight, among these reductive carbonylations, the direct route is obviously much more interesting than the other, since the carbamate cracking step can be avoided. Unfortunately, up to now much higher yields are achieved using the indirect reaction and therefore it appears very unlikely that the direct transformation will be exploited for isocyanate production in the present state of the art. Achievement of the direct reductive carbonylation with yields comparable to the indirect reaction would however render this approach much more appealing for industry [1,386].

Nowadays in order to replace the traditional phosgene-based manufacture, the essential requirements for a given catalytic system based on Group VIII metals can be summarized as follows: (i) very high activity and selectivity in the desired product, (ii) slight or negligible loss of efficiency upon repeated use i.e. slow deactivation, (iii) easy catalyst recovery after deactivation of the system. Then, considerations as (iv) availability from simple starting materials constitute important advantages, but much more importantly, (v) the process should not involve very poisonous components or generate toxic waste and possibly (vi) work in non-aggressive media.

5.2. *The well-known disadvantages of direct reaction*

As mentioned previously, the major drawback of most catalytic systems is their low efficiency for the direct carbonylation in comparison with indirect transformations. The decreased efficiency of direct carbonylation processes has been stated for a long time and was traditionally attributed to the high reactivity of the isocyanate formed [10]. Indeed, in these reactions, the yield in isocyanate reaches a maximum value before starting to decrease and contact time with the catalyst has to be maintained to a minimum value past this point in order to achieve optimal yields [98,155,169]. Follow-up reactions of the in situ generated isocyanate product leading mainly to the formation of tars were invoked to explain this observation. Accordingly, isocyanates are known to easily form various oligomers and polymers upon heating, especially in the presence of Lewis acid catalysts [130,131,387,388]. These undesirable polymerization reactions, which become clearly dominant above 200°C, were suspected to constitute an unavoidable drawback of the direct route [63,96,159]. To our knowledge, however, no comprehensive study in the current literature has ever addressed the problem of the deactivation pathways for typical nitroaromatic carbonylation catalysts. In fact, very little is known about the real chemistry underlying these detrimental process in direct carbonylation.

5.3. Deactivation pathways in the direct ([Pd]/phen/H^+) system

After the discovery of efficient catalysts for indirect carbonylation, attempts were made to extend these systems to the direct route [67,101,156]. Unfortunately, in most cases, these were less active or completely inactive in an inert solvent, urea usually being the main product formed when no alcohol was present. The Pd/phen and $PdCl_2$/heteropolyanion-based catalysts, however, constituted exceptions in the sense that these systems remained quite active under direct carbonylation conditions [156,158]. Investigations on the former system showed that slow deactivation of the catalyst took place in toluene[21]. Whereas ligand, temperature, CO pressure and promoter influence were roughly similar to the indirect reaction, a much larger excess of the carboxylic acid promoter needed to be present[22]. The main side products were *N*,*N′*-diphenylurea, isocyanate oligomers and uncharacterized polymers [156]. Subsequent work of Osborn et al., in the continuation of their mechanistic studies with this system allowed some insight in the deactivation pathways of this particular catalyst during direct carbonylation [129,366]. The isolation and structural characterization of metallacycles (K), (L) and (M) and elucidation of their chemistry indicated that these complexes could be formed from catalytic intermediates such as (I), by reaction with excess isocyanate (see Scheme 17). Compounds (L) and (M) can be seen as metal–imido species trapped by isocyanate [360,389]. Under conditions close to these used for the catalysis an easy interconversion between these metallacycles can take place. Thus, it is very likely that during the carbonylation, part of the active species will be converted into such species.

In the presence of a proton source, these metallacycles liberate diphenylurea or triphenylbiuret (see Scheme 17) [366]. These were precisely the byproducts formed

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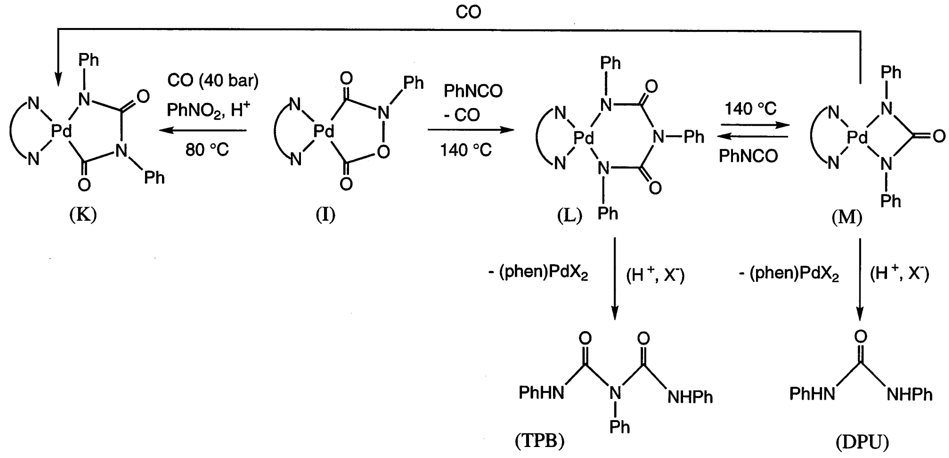
[21] Loss of selectivity was also stated when more polar solvent such as THF were used.

[22] Certain Brönsted acids (like *para*-toluenesulfonic acid or methanesulfonic acid), when used as co-catalysts, poisoned the system. Moreover, the choice of catalyst precursor was crucial, even in the presence of acid [156].



Scheme 17.

during the catalytical direct transformation and it appear therefore plausible that the urea (main side-product) formed during the direct carbonylation originated from similar metallacycles, by reaction with the carboxylic acid promoter. In that case, these protonolysis reactions should lead ultimately to the deactivation of the catalytic system by consumption of the acid co-catalyst, accordingly with what had been stated [158]. The formation of such metallacycles under catalytical conditions will also result in a lower effective concentration of the active species (I). This would in turn rationalize the decreased activity reported for the direct transformation relative to the indirect one and illustrates the crucial role played by alcohol in this reaction. Moreover, since any urea byproduced in the presence of alcohol will be alcoholized into the desired carbamate, the increase in carbamate-selectivity of the indirect transformation will be even more pronounced [35,43,46,70,100,121].

More generally, this study is quite informative since it confirms that in direct transformations, the isocyanate produced will not simply oligomerize or polymerize [155], but also that it can react with the catalyst and slowly deactivate it. Such a poisoning effect of isocyanate had already been reported in the literature without any clear explanation being given [171], and the data reported for a similar rhodium-based system would also be consistent with such a picture [112]. Now, a better knowledge on the stability of these metallacyclic compounds is desirable to ascertain this hypothesis and its generality.

5.4. Perspectives for direct carbonylation

We have seen in the previous sections concerned with the mechanisms of these carbonylation reactions (see notably Section 4) that with certain catalysts, addition of alcohol might have a profound influence on the reaction pathway taken by the transformation. When the mechanism is completely different, depending or not on the presence of alcohol, the decreased efficiency of catalytic systems for the direct carbonylation is not very surprising and has perhaps not much to do with the reactivity of free isocyanate. In such a case, improvement of the direct transformation may present no solution apart from switching to a new catalytic system more adapted to the direct route. This is possibly the case of the previously mentioned ruthenium or rhodium cluster-based catalysts which are essentially active under indirect conditions. However, there are apparently also catalysts for which quite similar mechanisms are operative regardless of the presence of alcohol. This may now be the case for Pd-derived systems such as (Pd/phen/H^+) and ($PdCl_2$/HPA) systems. Investigations conducted on the former system have shown that follow-up reactions of free isocyanate with the catalyst took place during the carbonylation and these are probably responsible for the decreased activity under direct conditions. Thus, if one could avoid follow-up reactions of the isocyanate with the catalyst, an activity comparable with the indirect process may be achieved under direct conditions.

This means that for any given catalytic system to be used under direct carbonylation conditions, investigation of the reactions between the catalyst precursor(s) and isocyanate will be crucial in order to delineate to what extent inhibition of the catalyst by isocyanate takes place, especially when reliable mechanistic information on the transformation is not available. Large improvement of the performances for systems active in the absence of alcohol may be achieved by preventing consecutive reaction of the isocyanate with the active species. Although difficult, this task could constitute the key to render direct carbonylation competitive with indirect carbonylation in terms of product yield. Alternatively, new active direct catalytic systems that will not react with the isocyanate may also be designed after a better knowledge of the reactivity of isocyanates with Group VIII metal centers will have been gained [229,389,390].

6. General conclusions

Mainly aroused by industrial interest, nitroaromatic carbonylation reactions have been extensively studied for 40 years now, as a means of replacing the traditional process for isocyanate production. Many catalytic systems have been found, the most active among them featuring Group VIII transition metals of the second period such as ruthenium, rhodium or palladium. As late as 1988 and despite the intense activity in this field, the lack of mechanistic insight in these catalytical reactions was evident. Nowadays, many additional studies have been conducted on this industrially appealing transformations, but on the whole, the mechanisms involved are still poorly understood and no general and unifying mechanism seems to emerge with Group VIII catalysts. Depending on the catalytic system used and on the presence or not of alcohol, many different catalytic cycles involving different types of intermediates were proposed for the carbonylation of nitroaromatics (I–VI). Important points of concern like the nuclearity of intermediates, the participation or not of a metal–imido intermediate to the catalytic cycle or the changes brought by introduction of alcohol in the medium (indirect carbonylation) are still unclear for most of the systems.

Despite being hardly competitive with the existing phosgene-based process, nitroaromatic reductive carbonylation reactions are worth consideration regarding environmental considerations. This is especially true for the direct approach. Improvement of the existing catalysts for the direct carbonylation appears however challenging and the little knowledge acquired to date has already pointed out some of the problems that will have to be overcome. First a clearer picture of the reaction mechanisms has to emerge, then a better knowledge of the reactions of isocyanate with the catalyst has to be gained. Notably, this means a better understanding of the interconversions between imido, amido and amino of Group VIII transition metal complexes and of their carbonylation reactions. Regardless of the elaboration of an efficient direct carbonylation process, these studies will also stimulate development of other practical applications in industry like the design of more interesting catalytic systems for the indirect way in regard to industrial exploitation (price and ease of recovery of catalyst, temperature control of the process, increased catalytic activity, etc.) or the improvement of related transformations (like oxidative carbonylation of amines or synthesis of ureas from nitroaromatics). Finally, on the fundamental side, a better understanding of these basic transformations of the nitro group is obviously attractive.

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References

[1] R.H. Richter, R.D. Priester Jr., in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 14, Wiley, New York, 1995, p. 905.
[2] K.C. Fritsch, D. Klempner, in: G. Allen, J.C. Bevington (Eds.), Comprehensive Polymer Science, vol. 5, Pergamon, New York, 1989, p. 413.
[3] A.J. Ryan, J.L. Stanford, in: G. Allen, J.C. Bevington (Eds.), Comprehensive Polymer Science, vol. 5, Pergamon, New York, 1989, p. 427.
[4] R.L. Metcalf, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 14, Wiley, New York, 1995, p. 570.
[5] T. Kato, K. Suzuki, J. Takahashi, K. Kamishota, J. Pesticide Sci. 9 (1984) 489.
[6] V.I. Manov-Yuvenskii, B.K. Nefedov, K.O. Khoshdurdyev, Russ. Chem. Bull. 31 (1982) 1176.
[7] N.N. Melinkov, Chemistry of Pesticides, Springer Verlag, Berlin, 1971, p. 183.
[8] G.S. Hartley, Chemicals for Pest Control, Pergamon, New York, 1969, p. 86, 174.

[9] D.K. Georges, D.H. Moore, W.P. Brian, J.S. Gorman, J. Agr. Food Chem. 2 (1954) 356.
[10] H.J. Twitchett, Chem. Soc. Rev. 3 (1974) 209.
[11] M. Aresta, E. Quaranta, Chemtech (1997) 32.
[12] K.L. Dunlap, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 18, Wiley, New York, 1995, p. 651.
[13] B. Hilleman, Chem. Eng. News (1993) 11.
[14] Chem. Week, March 9 (1977) 43.
[15] S. Fukuoka, M. Chono, M. Khono, Chemtech (1984) 670.
[16] S. Ozaki, Chem. Rev. 72 (1972) 457.
[17] H.-J. Knölker, T. Braxmeier, G. Schlechtingen, Angew. Chem. Int. Ed. Engl. 34 (1995) 2497.
[18] M.M. Mauri, U. Romano, F. Rivetti, Ing. Chim. Ital. 21 (1985) 6.
[19] F. Porta, S. Cenini, M. Pizzoti, C. Crotti, Gazz. Chim. Ital. 115 (1985) 275.
[20] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
[21] Y. Ono, Pure Appl. Chem. 68 (1996) 367.
[22] H. Eckert, B. Forster, Angew. Chem. Int. Ed. Engl. 26 (1987) 894.
[23] L. Cotarca, P. Delogu, A. Nardelli, V. Sunjic, Synthesis (1995) 553.
[24] T.E. Waldman, W.D. MacGhee, J. Chem. Soc. Chem. Commun. (1994) 957.
[25] M. Aresta, A. Dibenedetto, E. Quaranta, J. Chem. Soc. Dalton Trans. (1995) 3359.
[26] C. Bruneau, P.H. Dixneuf, J. Mol. Catal. 74 (1992) 97.
[27] W. MacGhee, D.P. Riley, M.E. Christ, K.M. Christ, Organometallics 12 (1993) 1429.
[28] W. MacGhee, D.P. Riley, Organometallics 11 (1992) 900.
[29] T. Tsuda, H. Washita, K. Watanabe, M. Miwa, T. Saegusa, J. Chem. Soc. Chem. Commun. (1978) 815.
[30] M. Aresta, E. Quaranta, Tetrahedron 47 (1991) 9489.
[31] W. MacGhee, D. Riley, K. Christ, X. Pan, B. Parnas, J. Org. Chem. 60 (1995) 2820.
[32] A.A. Kelkar, D.S. Kohle, S. Kanagasabhapathy, R.V. Chaudhari, Ind. Eng. Chem. Res. 31 (1992) 172.
[33] T. Watanabe, F. Yoshimoto, Petrotech 16 (1993) 544.
[34] F.J. Waller, J. Mol. Catal. 31 (1985) 123.
[35] S. Fukuoka, M. Chono, M. Khono, J. Chem. Soc. Chem. Commun. (1984) 399.
[36] S.A.R. Mulla, C.V. Rode, A.A. Kelkar, S.P. Gupte, J. Mol. Cat. A Chem. 122 (1997) 103.
[37] S.B. Halligudi, K.N. Bhatt, N.H. Khan, R.I. Kurashy, K. Venkatsubramanian, Polyhedron 15 (1996) 2093.
[38] I. Pri-Bar, J. Schwartz, J. Org. Chem. 60 (1995) 8124.
[39] V.L.K. Valli, H. Alper, Organometallics 14 (1995) 80.
[40] F.W. Hartstock, D.G. Herrington, L.B. MacMahon, Tetrahedron Lett. 35 (1994) 8761.
[41] S.A.R. Mulla, S.P. Gupte, R.V. Chaudhari, J. Mol. Catal. 67 (1991) L7.
[42] B.M. Choudary, K.R. Kumar, M.L. Kantam, J. Mol. Catal. 130 (1991) 141.
[43] P. Giannoccaro, C.F. Nobile, G. Moro, A. La Ginestera, C. Ferragina, M.A. Massucci, P. Patrono, J. Mol. Catal. 53 (1989) 349.
[44] S.P. Gupte, R.V. Chaudhari, J. Catal. 114 (1988) 246.
[45] H. Alper, G. Vasapollo, F.W. Hardstock, M. Mlekuz, D.J.H. Smith, G.E. Morris, Organometallics 6 (1987) 2391.
[46] P. Giannoccaro, Inorg. Chim. Acta 142 (1988) 81.
[47] H. Alper, F.W. Hartstock, J. Chem. Soc. Chem. Commun. (1985) 1141.
[48] J.J. Lindberg, B. Malm, L. Suomi, Finn. Chem. Lett. (1980) 153.
[49] E. Bolzachini, S. Meinardi, M. Orlandi, B. Rindone, J. Mol. Catal. A Chem. 111 (1996) 281.
[50] T.W. Leung, B.D. Dombeck, J. Chem. Soc. Chem. Commun. (1992) 205.
[51] F. Benedeti, S. Tollari, G. La Monica, M. Nali, S. Cenini, F. Porta, B. Rindone, J. Mol. Catal. 34 (1986) 155.
[52] M.M. Taqui-Khan, S.B. Halligudi, S. Skula, J. Mol. Catal. 59 (1990) 303.
[53] J.E. Mac Cusker, J. Logan, L. MacElwee-White, Organometallics 17 (1998) 4037.
[54] K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai, N. Sonoda, Angew. Chem. Int. Ed. Engl. 18 (1979) 692.

[55] M.A. Casadei, A. Inesi, F.M. Moracci, L. Rossi, J. Chem. Soc. Chem. Commun. (1996) 2575.
[56] S. Cenini, F. Ragaini, in: R. Ugo, B.R. James (Eds.), Reductive Carbonylation of Organic Nitro Compounds, Catalysis by Metal Complexes, Kluwer, Dordrecht, 1997.
[57] A.M. Tafesh, J. Weiguny, Chem. Rev. 96 (1996) 2035.
[58] F. Ragaini, S. Cenini, J. Mol. Catal. A Chem. 109 (1996) 1.
[59] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, second ed., Wiley, New York, 1992, p. 114.
[60] S. Cenini, C. Crotti, in: A.F. Noëls, M. Graziani, A.J. Hubert (Eds.), Catalysis by Metal Complexes. Metal promoted selectivity in Organic Synthesis, vol. 12, Kluwer, Dordrecht, 1991, p. 311.
[61] T. Ikariya, Catalysis 31 (1989) 271.
[62] S. Cenini, M. Pizzotti, C. Crotti, in: R. Ugo (Ed.), Aspects in Homogeneous Catalysis, vol. 6, Reidel, Dordrecht, 1988, p. 97.
[63] V.I. Manov-Yuvenskii, B.K. Nefedov, Russ. Chem. Rev. 50 (1981) 470.
[64] V.D. Selivanov, I.I. Konstatinov, Russ. J. Phys. Chem. 49 (1975) 620.
[65] T.P. Vishnyakova, I.A. Golubeva, E.V. Glebova, Usp. Khim. 54 (1985) 429 (Chem. Abs. 103: 21850n).
[66] F. Calderazzo, Inorg. Chem. 4 (1965) 293.
[67] A. Bassoli, B. Rindone, S. Cenini, J. Mol. Catal. 66 (1991) 163.
[68] P. Giannoccaro, E. Pannacciulli, Inorg. Chim. Acta 117 (1986) 69.
[69] H.A. Dieck, R.M. Laine, R.F. Heck, J. Org. Chem. 40 (1975) 5040.
[70] P. Giannoccaro, J. Organomet. Chem. 336 (1987) 271.
[71] J.S. Lee, C.W. Lee, S.M. Lee, K.H. Park, J. Mol. Catal. 61 (1990) L15.
[72] J.S. Oh, S.M. Lee, J.K. Yeo, C.W. Lee, J.S. Lee, Ind. Eng. Chem. Res. 30 (1991) 1456.
[73] S.M. Lee, N.S. Cho, K.D. Kim, J.S. Oh, C.W. Lee, J.S. Lee, J. Mol. Catal. 73 (1992) 43.
[74] K.D. Kim, S.M. Lee, N.S. Cho, J.S. Oh, C.W. Lee, J.S. Lee, J. Mol. Catal. 75 (1992) L1.
[75] C.W. Lee, S.M. Lee, J.S. Oh, J.S. Lee, Catal. Lett. 19 (1993) 217.
[76] V.L.K. Valli, H. Alper, J. Am. Chem. Soc. 115 (1993) 3778.
[77] K.D. Kim, J.S. Lee, K.H. Lee, Res. Chem. Intermed. 24 (1998) 197.
[78] Y. Tsuji, R. Takeuchi, Y. Watanabe, J. Organomet. Chem. 290 (1985) 249.
[79] A.G. Bayer, Patent EP 71 835, Germany, 1983.
[80] I.J.B. Lin, C.-S. Chang, J. Mol. Catal. 73 (1992) 167.
[81] M.Z.A. Badr, M.M. Aly, S.A. Mahgoub, A.A. Attallah, Rev. Roum. Chim. 37 (1992) 489.
[82] V.L.K. Valli, H. Alper, J. Org. Chem. 60 (1995) 257.
[83] D.C.D. Butler, H. Alper, Chem. Commun. (1998) 2575.
[84] O. Agherghinei, C. Prisacariu, A.A. Caraculacu, Rev. Roum. Chim. 36 (1991) 9.
[85] A.A. Caraculacu, I. Agerghinei, M. Gaspar, C. Prisacariu, J. Chem. Soc. Perkin Trans. (1990) 1343.
[86] D.P.N. Satchell, R.S. Satchell, Chem. Soc. Rev. 4 (1975) 231.
[87] G. Hazzard, S.A. Lammiman, N.L. Poon, D.P.N. Satchell, R.S. Satchell, J. Chem. Soc. Perkin Trans. II (1985) 1029.
[88] J.J. Tondeur, G. Vandendunghen, M. Watelet, Chim. Nouv. 10 (1992) 1148.
[89] K. Schwetlick, R. Noak, F. Stebner, J. Chem. Soc. Perkin Trans. II (1994) 599.
[90] P. Wehman, L. Borst, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Ber. Recl. 130 (1997) 13.
[91] P. Wehman, L. Borst, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Mol. Catal. A Chem. 112 (1996) 23.
[92] H. Tietz, K. Schwetlick, Z. Chem. 25 (1985) 149.
[93] L.V. Gorbunova, I.L. Knyazeva, E.A. Davydova, G.A. Abakumov, Bull. Acad. Sci. USSR Div. Chem. Sci. 29 (1980) 761.
[94] B.K. Nefedov, V.I. Manov-Yuvenskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 28 (1979) 2066.
[95] B.K. Nefedov, V.I. Manov-Yuvenskii, K.O. Khoshdurdyev, Bull. Acad. Sci. USSR Div. Chem. Sci. 27 (1978) 99.
[96] V.I. Manov-Yuvenskii, B.A. Redoshkin, B.K. Nefedov, G.P. Belyaeva, Bull. Acad. Sci. USSR Div. Chem. Sci. 29 (1980) 117.
[97] H. Tietz, K. Unferverth, K. Schwetlick, Z. Chem. 17 (1977) 368.

[98] B.K. Nefedov, V.I. Manov-Yuvenskii, K.O. Khoshduredyev, S.S. Novikov, Doklady Chem. (Proc. Acad. Sci. USSR) 232 (1976) 77.
[99] R. Ugo, R. Psaro, M. Pizzotti, P. Nardi, C. Dossi, A. Andretta, G. Caparella, J. Organomet. Chem. 417 (1991) 211.
[100] P. Wehman, G.C. Dol, E. Moorman, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 13 (1994) 4856.
[101] A. Bassoli, B. Rindone, S. Tollari, S. Cenini, C. Crotti, J. Mol. Catal. 60 (1990) 155.
[102] F. Ragaini, S. Cenini, A. Fumagalli, C. Crotti, J. Organomet. Chem. 428 (1992) 401.
[103] H. Lund, in: H. Lund, M.M. Baizer (Eds.), Organic Electrochemistry. An Introduction and a Guide, third ed., Marcel Dekker, New York, 1991, p. 411.
[104] V.I. Manov-Yuvenskii, K.B. Petrovski, A.L. Lapidus, Bull. Acad. Sci. USSR Div. Chem. Sci. 33 (1984) 543.
[105] A.L. Lapidus, V.I. Manov-Yuvenskii, K.B. Petrovskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 31 (1982) 2282.
[106] V.I. Manov-Yuvenskii, K.B. Petrovskii, A.L. Lapidus, Bull. Acad. Sci. USSR Div. Chem. Sci. 34 (1986) 1561.
[107] V.I. Manov-Yuvenskii, K.B. Petrovski, A.L. Lapidus, Bull. Acad. Sci. USSR Div. Chem. Sci. 34 (1985) 2486.
[108] V.I. Manov-Yuvenskii, K.B. Petrovski, A.L. Lapidus, Bull. Acad. Sci. USSR Div. Chem. Sci. 32 (1983) 546.
[109] R. Santi, A.M. Romano, F. Panella, C. Santini, J. Mol. Catal. A Chem. 127 (1997) 95.
[110] H. des Abbayes, H. Alper, J. Am. Chem. Soc. 99 (1977) 98.
[111] K. Januszkiewicz, H. Alper, J. Mol. Catal. 19 (1983) 139.
[112] F. Ragaini, S. Cenini, Organometallics 13 (1994) 1178.
[113] J.H. Saunders, R.J. Slocombe, Chem. Rev. 43 (1948) 203.
[114] B.G. Gowenlock, W. Lüttke, Q. Rev. 12 (1958) 321.
[115] Y. Shvo, D. Czarkie, J. Organomet. Chem. 368 (1989) 357.
[116] S. Cenini, M. Pizzotti, F. Porta, G. La Monica, J. Organomet. Chem. 88 (1975) 237.
[117] W. Beck, M. Bauder, G. La Monica, S. Cenini, R. Ugo, J. Chem. Soc. Part A (1971) 113.
[118] P. Escaffre, A. Thorez, P. Kalck, J. Mol. Catal. 33 (1985) 87.
[119] F. Metz (Rhône Poulenc), unpublished work.
[120] J.D. Gargulak, A.J. Berry, M.D. Noirot, W.L. Gladfelter, J. Am. Chem. Soc. 114 (1992) 8933.
[121] S. Cenini, C. Crotti, M. Pizzotti, F. Porta, J. Org. Chem. 53 (1988) 1243.
[122] K. Nomura, J. Mol. Catal. A Chem. 95 (1995) 203.
[123] A.F.M. Iqbal, Chemtech (1971) 372.
[124] R.G. Arnold, J.A. Nelson, J.J. Verbanc, Chem. Rev. 57 (1957) 47.
[125] K. von Werner, W. Beck, Chem. Ber. 104 (1971) 2907.
[126] K. von Werner, W. Beck, Chem. Ber. 105 (1972) 3947.
[127] B. Kühn, E. Henschell, Chem. Ber. 21 (1888) 504.
[128] F. Kurzer, Chem. Rev. 56 (1955) 95.
[129] F. Paul, J. Fischer, P. Ochsenbein, J.A. Osborn, to be published.
[130] R.P. Tiger, L.I. Sarynina, S.G. Entelis, Russ. Chem. Rev. 41 (1985) 774.
[131] A.K. Zhitinkina, N.A. Shibanova, O.G. Tarakhanov, Russ. Chem. Rev. 54 (1985) 1104.
[132] G.D. Buckley, N.H. Ray, J. Chem. Soc. (1949) 1154.
[133] G. Patent, Patent GP 441 179, Germany, 1925.
[134] J.E. Kmiecik, J. Org. Chem. 30 (1965) 2014.
[135] S. Murahashi, S. Horiie, J. Takashi, Nippon Kagaku Zasshi 79 (1958) 68.
[136] H. Alper, J.T. Edward, Can. J. Chem. 48 (1970) 1543.
[137] Patent FP 1379231 (1964).
[138] W.B. Hardy, R.P. Bennett, Tetrahedron Lett. 11 (1967) 961.
[139] W.S. Durell, J.H. Bateman, D.S. Weiditich, Chemtech (1978) 382.
[140] V. Macho, L. Voicek, L. Schmidtova, J. Terlandova, Coll. Czech. Chem. Commun. 57 (1992) 2605.
[141] V. Macho, M. Kucera, M. Kralik, J. Coll. Czech. Chem. Commun. 60 (1995) 514.

[142] V. Macho, M. Kralik, F. Halmo, J. Mol. Catal. A Chem. 109 (1996) 119.
[143] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Carbonylation-Direct Synthesis of Carbonyl Compounds, Plenum Press, New York, 1991, p. 227.
[144] A. Basu, S. Bhaduri, H. Khwaja, J. Organomet. Chem. 319 (1987) C28.
[145] S. Cenini, M. Pizzotti, C. Crotti, F. Ragaini, F. Porta, J. Mol. Catal. 49 (1988) 59.
[146] K. Unferverth, R. Höntsch, K. Schwetlick, J. Prakt. Chem. 321 (1979) 86.
[147] V.I. Manov-Yuvenskii, A.V. Smetanin, B.K. Nefedov, Bull. Acad. Sci. USSR Div. Chem. Sci. 30 (1981) 1813.
[148] B. Elleuch, Y. Ben Taarit, J.M. Basset, J. Kervennal, Angew. Chem. Int. Ed. Engl. 21 (1982) 687.
[149] F.J. Weigert, J. Org. Chem. 38 (1973) 1316.
[150] B.K. Nefedov, V.I. Manov-Yuvenskii, S.S. Novikov, Doklady Chem. (Proc. Acad. Sci. USSR) 234 (1977) 347.
[151] H. Tietz, K. Unferverth, K. Schwetlick, Z. Chem. 20 (1980) 411.
[152] H. Tietz, K. Schwetlick, Z. Chem. 25 (1985) 147.
[153] P. Braunstein, R. Bender, Organometallics 1 (1982) 1236.
[154] S.P. Gupte, R.V. Chaudhari, J. Mol. Catal. 34 (1986) 241.
[155] S.B. Halligudi, R.V. Chaudhari, W.L.K. Dorais, Ind. Eng. Chem. Process. Des. Dev. 23 (1984) 794.
[156] S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni, J. Mol. Catal. 64 (1991) 179.
[157] I.I. Moiseev, M.N. Vargaftig, T.V. Chernysheva, T.A. Stromnova, A.E. Gekham, G.A. Tsirkov, A.M. Makhlina, J. Mol. Catal. A Chem. 108 (1996) 77.
[158] Y. Izumi, Y. Satoh, K. Urabe, J. Mol. Catal. 72 (1992) 37.
[159] S.P. Gupte, R.V. Chaudhari, J. Mol. Catal. 24 (1984) 197.
[160] A.N. Niyazov, B.K. Nefedov, K.O. Khoshdundyev, V.I. Manov-Yuvenskii, Doklady Chem. (Proc. Acad. Sci. USSR) 258 (1981) 267.
[161] B.K. Nefedov, V.I. Manov-Yuvenskii, A.L. Chimishkyan, V.M. Englin, Kinet. Katal. 19 (1978) 1065 (Chem. Abs. 89: 179629z).
[162] H. Tietz, K. Unferverth, K. Schwetlick, Z. Chem. 20 (1980) 295.
[163] B.K. Nefedov, V.I. Manov-Yuvenskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 26 (1977) 2404.
[164] H. Tietz, K. Unferverth, K. Schwetlick, Z. Chem. 18 (1978) 98.
[165] H. Tietz, K. Unferverth, D. Sagasser, K. Schwetlick, Z. Chem. 18 (1978) 141.
[166] H. Tietz, K. Unferverth, K. Schwetlick, Z. Chem. 18 (1978) 217.
[167] H. Tietz, K. Unferverth, D. Sagasser, K. Schwetlick, Z. Chem. 19 (1979) 304.
[168] S.S. Novikov, B.K. Nefedov, V.I. Manov-Yuvenskii, B.F. Dzhervinski, A.L. Chimishkyan, A.V. Smetanin, G.V. Lysanova, E.M. Reznik, L.Z. Gockman, Dokl. Akad. Nauk. 247 (1979) 125 (Chem. Abs. 91: 211010v).
[169] G.A. Razuvaev, B.K. Nefedov, V.I. Manov-Yuvenskii, L.V. Gorbunova, N.N. Vavilina, A.L. Chimishkyan, A.V. Smetanin, Bull. Acad. Sci. USSR Div. Chem. Sci. 28 (1979) 2294.
[170] H. Tietz, K. Unferverth, K. Schwetlick, Z. Chem. 20 (1980) 256.
[171] V.I. Manov-Yuvenskii, B.K. Nefedov, A.V. Smetanin, Bull. Acad. Sci. USSR Div. Chem. Sci. 30 (1981) 1817.
[172] S.S. Novikov, V.I. Manov-Yuvenskii, A.V. Smetanin, B.K. Nefedov, Doklady Chem. (Proc. Acad. Sci. USSR) 251 (1980) 135.
[173] V.I. Manov-Yuvenskii, A.V. Smetanin, B.K. Nefedov, A.L. Chimishkyan, Kinet. Katal. 21 (1981) 1335 (Chem. Abs. 94: 29883s).
[174] H. Tietz, P. Neitzel, K. Schwetlick, S. Ruediger, Z. Chem. 24 (1984) 186.
[175] H. Tietz, K. Schwetlick, G. Keisel, Z. Chem. 25 (1985) 290.
[176] Y. Izumi, Y. Satoh, K. Urabe, Chem. Lett. (1990) 795.
[177] E. Bolzacchini, R. Lucini, S. Meinardi, M. Orlandi, B. Rindone, J. Mol. Catal. A Chem. 110 (1996) 227.
[178] J.H. Grate, D.R. Hamm, D.H. Valentine, Patent WO 86 05 178, Catalytica Associates; Haldor Topsoe A/S, PCT Int. Appl., 1986 (Chem. Abs. 106: 42356s).
[179] J.H. Grate, D.R. Hamm, D.H. Valentine Jr., Patent US 4 629 804, Catalytica Associates, USA, 1986 (Chem. Abs. 106: 119471b).

[180] M.M. Taqui-Khan, S.B. Halligudi, S. Skula, Z.A. Shaik, J. Mol. Catal. 57 (1990) 301.
[181] D.K. Mukherjee, B.K. Palit, C.R. Saha, J. Mol. Catal. 91 (1994) 19.
[182] C.V. Rode, S.P. Gupta, R.V. Chaudhari, C. Pirozhkov, A.L. Lapidus, J. Mol. Catal. 91 (1994) 195.
[183] T. Mizuno, H. Alper, J. Mol. Catal. A Chem. 121 (1997) 119.
[184] L.V. Gorbunova, I.L. Knyazeva, K.O. Khoshdurdyev, V.I. Manov-Yuvenskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 31 (1982) 1334.
[185] (a) B.K. Nefedov, V.I. Manov-Yuvenskii, V.A. Semikolenov, V.A. Likholobov, Yu I. Ermakov, Kinet. Katal. 23 (1981) 1001. (b) A.L. Lapidus, A.F. Lunin, S.D. Pirozhkov, N.B. Leonchik, P. Neittzel, K. Shvetlick, Bull. Acad. Sci. USSR Div. Chem. Sci. 31 (1982) 1068.
[186] A.N. Niyazov, B.K. Nefedov, K.O. Khoshdundyev, V.I. Manov-Yuvenskii, Doklady Chem. (Proc. Acad. Sci. USSR) 258 (1981) 242.
[187] S.B. Halligudi, N.H. Khan, R.I. Kureshy, E. Suresh, K. Venkatsubramanian, J. Mol. Catal. A Chem. 124 (1997) 147.
[188] P. Wehman, V.E. Kaasjager, W.G.J. de Lange, F. Hartl, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 14 (1995) 3751.
[189] P. Wehman, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Chem. Soc. Chem. Commun. (1996) 217.
[190] A. Bontempi, E. Alessio, G. Chanos, G. Mestroni, J. Mol. Catal. 42 (1987) 67.
[191] B.M. Choudary, K.K. Rao, S.D. Pirozhkov, A.L. Lapidus, J. Mol. Catal. 88 (1994) 23.
[192] N.P. Reddy, A.M. Masdeu, B.E. Ali, H. Alper, J. Chem. Soc. Chem. Commun. (1994) 863.
[193] Y. Watanabe, Y. Tsuji, R. Takeuchi, N. Suzuki, Bull. Chem. Soc. Jpn. 56 (1983) 3343.
[194] E. Alessio, G. Mestroni, J. Organomet. Chem. 291 (1985) 117.
[195] E. Drent, Patent EP 231045, Shell International Research, 1987.
[196] A.R. Tumanova, S.D. Pirozhkov, A.L. Lapidus, Khim. Tverd. Topl. (Moscow) (1992) 55 (Chem. Abs. 117: 253854j).
[197] L.V. Gorbunova, I.L. Knyazeva, B.K. Nefedov, K.O. Khoshdundyev, V.I. Manov-Yuvenskii, Izv. Akad. Nauk. SSSR Ser. Khim. (1988) 1644 (Chem. Abs. 95 115000d).
[198] Y. Watanabe, Y. Tsuji, N. Suzuki, Chem. Lett. (1982) 105.
[199] S. Cenini, M. Pizzotti, C. Crotti, F. Porta, G. La Monica, J. Chem. Soc. Chem. Commun. (1984) 1286.
[200] E. Drent, Pure Appl. Chem. 62 (1990) 661.
[201] C.W. Lee, J.S. Lee, S.M. Lee, K.D. Kim, N.S. Cho, J.S. Oh, J. Mol. Catal. 81 (1993) 17.
[202] S.J. Sherlock, D.C. Boyd, B. Moasser, W.L. Gladfelter, Inorg. Chem. 30 (1991) 3626.
[203] J.D. Gargulak, M.D. Noirot, W.L. Gladfelter, J. Am. Chem. Soc. 113 (1991) 1054.
[204] A.J. Kunin, M.D. Noirot, W.L. Gladfelter, J. Am. Chem. Soc. 111 (1989) 2739.
[205] J.D. Gargulak, W.L. Gladfelter, J. Am. Chem. Soc. 116 (1994) 3792.
[206] S.J. Skoog, J.P. Campbell, W.L. Gladfelter, Organometallics 13 (1994) 4137.
[207] E. Drent, P.W.N.M. van Leeuwen, Patent EP 86281, Shell International Research, 1981.
[208] E. Alessio, G. Mestroni, Patent EP 0169650, Montedison, 1985.
[209] E. Drent, Patent EP 224292, Shell International Research, 1987.
[210] E. Alessio, G. Mestroni, J. Mol. Catal. 26 (1984) 237.
[211] F. Zhang, W. Wang, W. Huang, R. Long, P. Xu, J. Xu, Xiamen Daxue Xuebao, Ziran Kuxueban 32 (1993) 177 (Chem. Abs. 121: 107754).
[212] F. Zhang, W. Wang, P. Xu, J. Xu, Fenzi Cuihua 5 (1991) (Chem. Abs. 116: 128307).
[213] G. Clauti, G. Zassinovich, G. Mestroni, Inorg. Chim. Acta 112 (1986) 103.
[214] F. Ragaini, M. Macchi, S. Cenini, J. Mol. Catal. A Chem. 127 (1997) 33.
[215] J.S. Lee, J.W. Woo, C.W. Lee, K.S. Hong, J.K. Yeo, Korean J. Chem. Eng. 7 (1990) 145.
[216] P. Leconte, F. Metz, A. Mortreux, J.A. Osborn, F. Paul, F. Petit, A. Pillot, J. Chem. Soc. Chem. Commun. (1990) 1616.
[217] T. Kajimoto, J. Tsuji, Bull. Chem. Soc. Jpn. 42 (1969) 827.
[218] (a) K. Unferverth, K. Schwetlick, React. Kinet. Catal. Lett. 6 (1977) 231. (b) K. Unferverth, R. Höntsch, K. Schwetlick, J. Prakt. Chem. 321 (1979) 928.
[219] K. Unferverth, H. Tietz, K. Schwetlick, J. Prakt. Chem. 327 (1985) 932.

[220] S.S. Novikov, V.I. Manov-Yuvenskii, A.V. Smetanin, B.K. Nefedov, Bull. Acad. Sci. USSR Div. Chem. Sci. 29 (1980) 135.
[221] V.A. Melhorn, C. Rüger, K. Schwetlick, J. Prakt. Chem. 317 (1975) 575.
[222] V.A. Melhorn, C. Rüger, K. Schwetlick, J. Prakt. Chem. 317 (1975) 583.
[223] V.A. Melhorn, C. Rüger, K. Schwetlick, J. Prakt. Chem. 317 (1975) 867.
[224] B.K. Nefedov, V.I. Manov-Yuvenskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 28 (1979) 540.
[225] E. Sappa, L. Milone, J. Organomet. Chem. 61 (1973) 383.
[226] H. Alper, H.-N. Paik, Nouv. J. Chim. 2 (1977) 245.
[227] M. Dekker, G.R. Knox, J. Chem. Soc. Chem. Commun. (1967) 1243.
[228] S. Aime, G. Gervasio, L. Milone, R. Rossetti, P.L. Stanghellini, J. Chem. Soc. Dalton Trans. (1978) 534.
[229] A.N. Nesmeyanov, M.I. Ribinskaya, L.V. Rybin, Russ. Chem. Rev. 48 (1979) 393.
[230] S. Bhaduri, A. Chatterjee, S. Pal, S. Tawde, D. Mukesh, Proc. Indian Acad. Sci. Chem. Sci. 108 (1996) 495.
[231] S. Bhaduri, K.S. Gopalkrishnon, B.S. Sheldrik, W. Clegg, D. Stalke, J. Chem. Soc. Dalton Trans. (1983) 2339.
[232] S. Bhaduri, H. Khwaja, P.G. Jones, J. Chem. Soc. Chem. Commun. (1988) 194.
[233] S. Bhaduri, H. Khwaja, N. Sapre, K. Sharma, A. Basu, P.G. Jones, G. Carpenter, J. Chem. Soc. Dalton Trans. (1990) 1313.
[234] C. Crotti, S. Cenini, R. Todeschini, S. Tollari, J. Chem. Soc. Faraday Trans. (1991) 2811.
[235] C.-H. Liu, C.-H. Cheng, J. Organomet. Chem. 420 (1991) 119.
[236] F. L'Eplattenier, P. Matthys, F. Calderazzo, Inorg. Chem. 9 (1970) 343.
[237] R. Koelliker, G. Bor, J. Organomet. Chem. 417 (1991) 439.
[238] S.H. Han, J.-S Dong, P.D. Macklin, S.T. Nguyen, G.L. Geoffroy, A.L. Reingold, Organometallics 13 (1989) 2127.
[239] G.D. Williams, R.R. Whittle, G.L. Geoffroy, A.L. Reingold, J. Am. Chem. Soc. 109 (1987) 3936.
[240] S.-H. Han, G.L. Geoffroy, A.L. Reingold, Inorg. Chem. 26 (1987) 3426.
[241] D.L. Ramage, G.L. Geoffroy, A.L. Reingold, B.S. Haggerty, Organometallics 11 (1992) 1242.
[242] T. Chin-Choy, W.T.A. Harrison, G.D. Stucky, N. Keder, P.C. Ford, Inorg. Chem. 28 (1989) 2028.
[243] S.-H. Han, G.L. Geoffroy, Polyhedron 7 (1988) 2331.
[244] J. Lillis, A. Rokicki, T. Chin, P.C. Ford, Inorg. Chem. 32 (1993) 5040.
[245] S. Rivomanana, G. Lavigne, N. Lugan, J.-J. Bonnet, Organometallics 10 (1991) 2285.
[246] F. Ragaini, S.-L. Song, D.L. Ramage, G.L. Geoffroy, Organometallics 14 (1995) 387.
[247] M. Pizzotti, S. Cenini, S. Quici, S. Tollari, J. Chem. Soc. Perkin Trans. II (1994) 913.
[248] E. Alessio, F. Vinzi, G. Mestroni, J. Mol. Catal. 22 (1984) 327.
[249] E. Alessio, G. Zassinovitch, G. Mestroni, J. Mol. Catal. 18 (1983) 113.
[250] S.J. Skoog, W.L. Gladfelter, J. Am. Chem. Soc. 119 (1997) 11049.
[251] J.D. Gargulak, R.D. Hoffman, W.L. Gladfelter, J. Mol. Catal. 68 (1991) 289.
[252] M.M. Taqui Khan, Platin. Met. Rev. 35 (1991) 70.
[253] F. Ragaini, S. Cenini, F. Demartin, J. Chem. Soc. Chem. Commun. (1992) 1467.
[254] P.-H. Liu, H.-Y. Liao, C.-H. Cheng, J. Chem. Soc. Chem. Commun. (1995) 2441.
[255] F. Ragaini, S. Cenini, J. Mol. Catal. A Chem. 105 (1996) 145.
[256] U. Kiiski, T. Venäläinen, T.A. Pakanen, J. Mol. Catal. 64 (1991) 163.
[257] G. Schmid, Polyhedron 7 (1988) 2321.
[258] M.N. Vargaftik, I.I. Moiseev, D.I. Kochubey, K.I. Zamarev, Faraday Discuss. Chem. Soc. 92 (1991) 1.
[259] F. Paul, J. Fischer, P. Ochsenbein, J.A. Osborn, Organometallics 17 (1998) 2199.
[260] A.S. o Santi, B. Milani, G. Mestroni, L. Randaccio, J. Organomet. Chem. 545–546 (1997) 89.
[261] N. Masciocchi, F. Ragaini, S. Cenini, A. Sironi, Organometallics 17 (1998) 1052.
[262] H. Werner, U. Brekau, O. Nürnberg, B. Zeier, J. Organomet. Chem. 440 (1992) 389.
[263] P.A. Chetcuti, K.B. Knobler, M.F. Hawthorne, Organometallics 7 (1988) 650.
[264] A. Pillot-Scotte, A Mortreux, unpublished results.
[265] G. Cavinato, L. Toniolo, J. Organomet. Chem. 444 (1993) C65.
[266] J.E. Byrd, J. Halpern, J. Am. Chem. Soc. 93 (1971) 1634.

[267] R.J. Angelici, Acc. Chem. Res. 5 (1972) 335.
[268] C.R. Green, R.J. Angelici, Inorg. Chem. 11 (1972) 2095.
[269] F. Lefebvre, P. Gelin, B. Elleuch, C. Naccache, Y. Ben Taarit, Bull. Chim. Soc. Fr. (1984) 361.
[270] I.I. Moiseev, M.N. Vargaftik, New. J. Chem. (1998) 1217.
[271] I.I. Moiseev, T.A. Stromnova, M.N. Vargaftik, Bull. Acad. Sci. USSR Div. Chem. Sci. 47 (1998) 777.
[272] G. Bor, Pure Appl. Chem. 58 (1986) 543.
[273] R.S. Berman, J.K. Kochi, Inorg. Chem. 19 (1980) 248.
[274] A. Alberti, C.M. Camaggi, J. Organomet. Chem. 194 (1980) 343.
[275] Y.A. Belousov, T.A. Kolosova, Polyhedron 6 (1987) 1959.
[276] E.K. von Gustorf, M.C. Henry, R.E. Sacher, C. Di Pietro, Z. Naturforsch. 21B (1966) 1152.
[277] E.K. von Gustorf, Angew. Chem. Int. Ed. Engl. 5 (1966) 739.
[278] F. Ragaini, S. Cenini, S. Tollari, G. Tummolillo, R. Beltrami, Organometallics 18 (1999) 928.
[279] H. Alper, G. Vasapollo, Tetrahedron Lett. 28 (1987) 6411.
[280] F. Porta, M. Pizzotti, S. Cenini, J. Organomet. Chem. 222 (1981) 279.
[281] K. Unferverth, C. Rüger, K. Schwetlick, J. Prakt. Chem. 319 (1977) 841.
[282] K. Unferverth, J. Pelz, F. Flemming, K. Schwetlick, Z. Chem. 14 (1974) 304.
[283] J. Pelz, K. Unferverth, K. Schwetlick, Z. Chem. 13 (1973) 288.
[284] D.W. Hoard, P.R. Sharp, Inorg. Chem. 32 (1993) 612.
[285] M. Pizzotti, F. Porta, S. Cenini, F. Demartin, N. Masciocchi, J. Organomet. Chem. 330 (1987) 265.
[286] G. Vasapollo, C.F. Nobile, P. Giannoccaro, F. Allegretta, J. Organomet. Chem. 277 (1984) 417.
[287] G. Vasapollo, P. Giannoccaro, C.F. Nobile, F. Allegretta, J. Organomet. Chem. 270 (1984) 109.
[288] L. Dahlenburg, C. Prengel, Inorg. Chim. Acta 122 (1986) 55.
[289] J.A. Smieja, W.L. Gladfelter, Inorg. Chem. 25 (1986) 2667.
[290] C. Crotti, S. Cenini, A. Bassoli, B. Rindone, F. Demartin, J. Mol. Catal. 70 (1991) 175.
[291] K.K.H. Lee, W.T. Wong, J. Chem. Soc. Dalton Trans. (1996) 3911.
[292] T.A. Stromnova, S.T. Orlova, I.P. Stolyarov, S.B. Katser, I.I. Moiseev, Doklady Chem. 352 (1997) 7.
[293] I.L. Eremenko, S.E. Nefedov, A.A. Sidorov, M.O. Ponina, P.V. Danilov, T.A. Stromnova, I.P. Stolarov, S.B. Katser, S.T. Orlova, M.N. Vargaftik, I.I. Moiseev, Y.A. Ustynyuk, J. Organomet. Chem. 551 (1998) 171.
[294] L. Chen, M.A. Khan, G.B. Richter-Addo, V.G. Young Jr., D.R. Powell, Inorg. Chem. 37 (1998) 4689.
[295] G. Matsubayashi, K. Nakatsu, Inorg. Chim. Acta 64 (1982) L163.
[296] L.-S. Wang, L. Chen, M.A. Khan, G.B. Richter-Addo, J. Chem. Soc. Chem. Commun. (1996) 323.
[297] P. Fantucci, M. Pizzotti, F. Porta, Inorg. Chem. 30 (1991) 2277.
[298] S. Otsuka, Y. Aotani, Y. Tatsuno, T. Yoshida, Inorg. Chem. 15 (1976) 657.
[299] M.J. Barrow, O.S. Mills, Angew. Chem. Int. Ed. Engl. 8 (1969) 879.
[300] W. Li, C.L. Barnes, P.R. Sharp, J. Chem. Soc. Chem. Commun. (1990) 1634.
[301] J.J. Li, P.R. Sharp, Inorg. Chem. 33 (1994) 183.
[302] A. Cervilla, A. Corma, V. Fornés, E. Llopis, F. Pérez, F. Rey, A. Ribera, J. Am. Chem. Soc. 117 (1995) 6781.
[303] H. Alper, J.-F. Petrignani, F.W.B. Einstein, A.C. Willis, J. Am. Chem. Soc. 105 (1983) 1701.
[304] J.-F. Petrignani, H. Alper, Inorg. Chim. Acta 77 (1983) L243.
[305] J. Fletcher, G. Hogarth, D.A. Tocher, J. Organomet. Chem. 403 (1991) 345.
[306] E.A. Maatta, R.A.D. Wentworth, Inorg. Chem. 19 (1979) 2597.
[307] J. Fawcett, J.H. Holloway, E.G. Hope, D.R. Russel, G.C. Sauders, M.J. Atherton, J. Organomet. Chem. 464 (1994) C20.
[308] W.J. Boyle Jr., F. Mares, Organometallics 1 (1982) 1003.
[309] W.H. Smith, A.J. Bard, J. Am. Chem. Soc. 97 (1975) 5203.
[310] A.F.M. Iqbal, Chemtech (1974) 566.
[311] J.A. Smieja, J.E. Gozum, W.L. Gladfelter, Organometallics 6 (1987) 1311.
[312] J.A. Smieja, J.E. Gozum, W.L. Gladfelter, Organometallics 5 (1986) 2154.

[313] S. Cenini, G. La Monica, Inorg. Chim. Acta 18 (1976) 279.
[314] R.P. Bennett, W.B. Hardy, J. Am. Chem. Soc. 90 (1968) 3295.
[315] G. La Monica, G. Ardizzoia, G. Maddinelli, S. Tollari, J. Mol. Catal. 38 (1986) 327.
[316] G. La Monica, C. Monti, S. Cenini, B. Rindone, J. Mol. Catal. 23 (1984) 89.
[317] G. La Monica, C. Monti, S. Cenini, J. Mol. Catal. 18 (1983) 93.
[318] G. La Monica, C. Monti, S. Cenini, J. Mol. Catal. 18 (1983) 83.
[319] G. La Monica, C. Monti, S. Cenini, J. Organomet. Chem. 216 (1981) C35.
[320] A.F.M. Iqbal, Helv. Chim. Acta 59 (1976) 655.
[321] A.N. Nesmeyanov, M.I. Ribinskaya, E.A. Petrovskaya, P.V. Petrovskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 20 (1972) 1873.
[322] T.A. Manuel, Inorg. Chem. 3 (1964) 1703.
[323] C. Crotti, S. Cenini, B. Rindone, S. Tollari, F. Demartin, J. Chem. Soc. Chem. Commun. (1986) 785.
[324] T. Izumi, M. Soutome, T. Miura, J. Heterocycl. Chem. 29 (1992) 1625.
[325] S. Cenini, S. Console, C. Crotti, S. Tollare, J. Organomet. Chem. 451 (1993) 157.
[326] Y. Watanabe, J. Yamamoto, M. Akazome, T. Kondo, T. Mitsudo, J. Org. Chem. 60 (1995) 8328.
[327] S. Tollari, S. Cenini, F. Ragaini, L. Cassar, J. Chem. Soc. Chem. Commun. (1994) 1741.
[328] C. Crotti, S. Cenini, F. Ragani, F. Porta, S. Tollari, J. Mol. Catal. 72 (1992) 283.
[329] A. Bassoli, S. Cenini, F. Farina, M. Orlandi, B. Rindone, J. Mol. Catal. 89 (1994) 121.
[330] F. Ragaini, S. Tollari, S. Cenini, E. Bettetini, J. Mol. Catal. A Chem. 105 (1996) 91.
[331] M. Akazome, T. Kondo, Y. Watanabe, J. Chem. Soc. Chem. Commun. (1991) 1467.
[332] M. Pizzotti, S. Cenini, P. Rinaldo, S. Costanzi, J. Mol. Catal. 63 (1991) 299.
[333] M. Akazome, T. Kondo, Y. Watanabe, Chem. Lett. (1992) 769.
[334] M. Akazome, T. Kondo, Y. Watanabe, J. Org. Chem. 58 (1993) 310.
[335] M. Akazome, T. Kondo, Y. Watanabe, J. Org. Chem. 59 (1994) 3375.
[336] M. Akazome, J. Yamamoto, T. Kondo, Y. Watanabe, J. Organomet. Chem. 494 (1995) 229.
[337] S. Cenini, E. Bettettini, M. Fedele, S. Tollari, J. Mol. Catal. A Chem. 111 (1996) 37.
[338] S. Tollari, S. Cenini, C. Crotti, E. Gianella, J. Mol. Catal. 87 (1994) 203.
[339] Y. Watanabe, Y. Tsuji, T. Kondo, R. Takeuchi, J. Org. Chem. 49 (1984) 4451.
[340] G. Smolinski, B.I. Feuer, J. Org. Chem. 31 (1966) 3882.
[341] S. Cenini, F. Ragaini, S. Tollari, D. Paone, J. Am. Chem. Soc. 118 (1996) 11964.
[342] A.F.M. Iqbal, Helv. Chim. Acta 55 (1972) 798.
[343] A.F.M. Iqbal, J. Org. Chem. 37 (1972) 2791.
[344] T. Cole, R. Ramage, K. Cann, R. Pettit, J. Am. Chem. Soc. 102 (1980) 6182.
[345] R.C. Ryan, G.M. Wilemon, M.P. Dalsanto, C.U. Pittman, J. Mol. Catal. 5 (1979) 319.
[346] Z. Yu, S. Liao, Y. Xu, B. Yang, D. Yu, J. Chem. Soc. Chem. Commun. (1995) 1155.
[347] E. Alessio, G. Clauti, G. Mestroni, J. Mol. Catal. 29 (1985) 77.
[348] K. Kaneda, K. Fujita, T. Takemoto, T. Imanaka, Bull. Chem. Soc. Jpn. 64 (1991) 602.
[349] K. Nomura, J. Mol. Catal. 78 (1993) 273.
[350] K. Kaneda, K. Kuwahara, T. Imanaka, J. Mol. Catal. 88 (1994) L267.
[351] F. Ragaini, S. Cenini, J. Mol. Catal. A Chem. 105 (1996) 145.
[352] F. Ragaini, M. Pizzotti, S. cenini, A. Abbotto, G. Demartin, J. Organomet. Chem. 489 (1995) 107.
[353] A. Tafesh, M. Beller, Tetrahedron Lett. 36 (1995) 9305.
[354] Y. Watanabe, Y. Tsuji, T. Ohsumi, R. Takeuchi, Tetrahedron Lett. 24 (1983) 4121.
[355] S. Bhaduri, K.S. Gopalkrishnon, W. Clegg, P.G. Jones, B.S. Sheldrik, D. Stalke, J. Chem. Soc. Dalton Trans. (1984) 1765.
[356] O.C. Beers, J.G.P. Delis, W.P. Mul, K. Vrieze, C.J. Elsevier, Inorg. Chem. 32 (1993) 3640.
[357] Y.-W. Ge, P.R. Sharp, Inorg. Chem. 31 (1992) 379.
[358] A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, Polyhedron 22 (1992) 2961.
[359] D.S. Glueck, J. Wu, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 113 (1991) 2041.
[360] R.I. Michelman, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 113 (1991) 5100.
[361] A.K. Burrell, A.J. Steedman, Organometallics 1997 (1995) 1203.
[362] D.E. Wigley, Prog. Inorg. Chem. 42 (1994) 239.
[363] T.A. Hanna, A.M. Baranger, R.G. Bergman, Angew. Chem. Int. Ed. Eng. 35 (1996) 653.

[364] F. Demartin, M. Pizzotti, F. Porta, S. Cenini, J. Chem. Soc. Dalton. Trans. (1987) 605.
[365] S. Cenini, F. Porta, M. Pizzotti, C. Crotti, J. Chem. Soc., Dalton Trans. (1985) 163.
[366] F. Paul, J. Fischer, P. Ochsenbein, J.A. Osborn, Angew. Chem. Int. Ed. Engl. 32 (1993) 1638.
[367] S. Bhaduri, H. Khwaja, K. Sharma, P.G. Jones, J. Chem. Soc. Chem. Commun. (1989) 515.
[368] H.A. Alper, K.E. Hashem, J. Am. Chem. Soc. 103 (1981) 6514.
[369] G. Mestroni, G. Zassinovich, E. Alessio, M. Tornatore, J. Mol. Catal. 49 (1989) 175.
[370] A.L. Lapidus, S.D. Pirozhkov, A.R. Tumanova, A.V. Dolidze, A.M. Yukhimenko, Bull. Acad. Sci. USSR Div. Chem. Sci. 41 (1992) 1672.
[371] G. Vasapollo, G. Toniolo, G. Cavinato, F. Bigoli, M. Lanfranchi, M.A. Dellinghelli, J. Organomet. Chem. 481 (1994) 173.
[372] P. Giannoccaro, L. Tommasi, M. Aresta, J. Organomet. Chem. 476 (1994) 13.
[373] P. Giannoccaro, J. Organomet. Chem. 470 (1994) 249.
[374] P. Giannoccaro, N. Ravasio, M. Aresta, J. Organomet. Chem. 451 (1993) 243.
[375] G. Vasapollo, C.F. Nobile, A. Sacco, Inorg. Chim. Acta 83 (1984) 125.
[376] G. Vasapollo, C.F. Nobile, A. Sacco, J. Organomet. Chem. 296 (1985) 435.
[377] J.H. Grate, D.R. Hamm, D.H. Valentine, Patent WO 86 05 179, Catalytica Associates; Haldor Topsoe, PCT Int. Appl., 1986 (Chem. Abs. 106: 32090c).
[378] P. Leconte, F. Metz, Patent EP 330 591, Rhône-Poulenc Chimie, 1989 (Chem. Abs. 112: 78160c).
[379] Chementator, Chem. Eng. News (1977) 73.
[380] Chem. Week, July 26 (1978) 28.
[381] Chem. Eng. News, Oct. 10 (1977) 12.
[382] J.W. Frost, K.M. Draths, Chem. Br. 3 (1995).
[383] I. Awato, Science 259 (1993) 1538.
[384] J.A. Cusumano, Chemtech (1992) 482.
[385] R.A. Sheldon, Chemtech (1994) 38.
[386] R. Pierantozzi, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 5, Wiley, New York, 1995, p. 107.
[387] J.-S. Tang, J.G. Verkade, Angew. Chem. Int. Ed. Eng. 32 (1993) 896.
[388] K. Schwetlick, R. Noack, J. Chem. Soc. Perkin Trans. II (1995) 395.
[389] W.-H. Leung, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1991) 2791.
[390] P. Braunstein, D. Nobel, Chem. Rev. 89 (1989) 1427.