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Pd-catalysed oxidative carbonylation of amino alcohols to *N,N′*-bis(hydroxyalkyl)ureas under mild conditions using molecular oxygen as the oxidant

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ABSTRACT

A very simple method has been developed for the selective synthesis of symmetrical *N,N′*-bis(hydroxyalkyl)ureas, OC[NH-$(CH_2)_x$-OH]$_2$ (x = 3–6), by oxidative carbonylation of α,ω-amino alcohols [3-aminopropanol (3-AP), 4-aminobutanol (4-AB), 5-aminopentanol (5-APe), 6-aminohexanol (6-AH)] with CO/O_2 mixtures (O_2 = 5 mol%) in the presence of Pd(II)/ligand/NEt_3·HI catalytic systems. The catalytic process takes place under very mild conditions ($p(CO/O_2)$ = 0.1 MPa; 303–333 K). The target products can be isolated in high yield through a very simple and straightforward procedure. The catalytic system can be easily recovered and recycled for several times.

The influence of a few reaction parameters (nature of ancillary ligand and iodide co-catalyst, I/Pd molar ratio, etc.) on the catalytic activity has also been investigated and the main mechanistic features of the catalytic process fully elucidated.

1. Introduction

Oxidative carbonylation of β-amino alcohols to afford oxazolidin-2-ones is a topic of current interest due to the remarkable biological activity exhibited by five-membered cyclic carbamates [1]. Both homogeneous [2] and heterogeneous [3] catalytic systems have been described for this process, which, depending on the nature of the catalyst used, can be accomplished under either mild or drastic conditions. In comparison, oxidative carbonylation of non-vicinal amino alcohols has received much poorer attention, despite its potential for the direct synthesis of *N,N′*-bis(hydroxyalkyl)ureas rather than cyclic carbamates.

N,N′-bis(hydroxyalkyl)ureas are useful compounds which find practical application in several fields [4]. Most of *N,N′*-bis(hydroxyalkyl)ureas can be prepared in a poorly selective way by direct reaction of non-vicinal amino alcohols with phosgene (Scheme 1) [4a,b], a toxic hazardous reagent whose utilization in chemical industry finds larger and larger constraints due to governmental policies for environmental protection. Environmentally more friendly synthetic protocols, based on the reaction of amino alcohols with less toxic phosgene-equivalents (1,1-carbonyldiimidazole, dimethyl ditiocarbonate [5], dimethyl- or diethyl carbonate [6]), are also available, but they often involve multistep procedures aimed at protecting the OH functional group in order to avoid the side-formation of carbamates and carbonates (Scheme 1).

Only recently *N,N′*-bis(hydroxyalkyl)ureas have been prepared by oxidative carbonylation of amino alcohols. Diaz et al. used $W(CO)_6$ as catalyst and stoichiometric amounts of I_2 as the oxidant, under a CO pressure as high as 8 MPa [7]: co-generation of large amounts of iodide salts, as well as tedious work-up of reaction crude, was a serious drawback of the process.

As a part of our studies on the reactivity of key intermediates in the oxidative carbonylation of alcohols [8,9], diols [10] and amines [11], we have recently found that a few L_nPdCl_2 complexes can promote the carbonylation of amino alcohols (NH_2-$(CH_2)_x$-OH) to cyclic carbamates and/or *N,N′*-bis(hydroxyalkyl)ureas and demonstrated that these reactions proceed through the intermediate formation of carbamoyl complexes L_nPdCl[C(O)NH-$(CH_2)_x$-OH] [12]. In general, these species exhibit very modest stability, but the complexes with triphenylphosphine ligand are fairly stable, and have been isolated, characterized and studied for their reactivity. Scheme 2 shows that the complexes $PdCl(PPh_3)_2$[C(O)NH-$(CH_2)_x$-OH] are thermally unstable and can decompose ($T > 303$ K) by generating a Pd(0)-intermediate, "$Pd(PPh_3)_2$", and a very reactive chloroformamide, ClC(O)NH-$(CH_2)_x$-OH, which, depending on the reaction conditions and the amino alcohol used, can afford either cyclic carbamates or *N,N′*-bis(hydroxyalkyl)ureas. According to whether the decomposition was carried out under N_2 or CO

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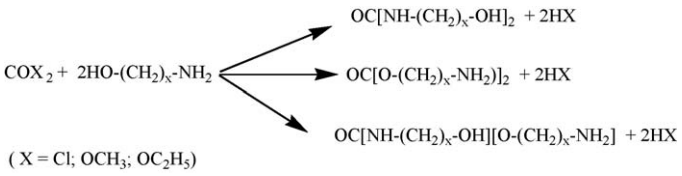


Scheme 1. Carbonylation of amino alcohols with phosgene or phosgene-equivalents.

atmosphere, the palladium(0)-intermediate, "$Pd(PPh_3)_2$", may further react in the reaction mixture by converting, into Pd(0)-carbonyl complexes and/or palladium metal, respectively. Remarkably, in the presence of a suitable oxidant, the latter species can be easily reoxidized to Pd(II), which in the presence of free amino alcohol and CO can regenerate the starting carbamoyl complex, $L_nPdCl[C(O)NH\text{-}(CH_2)_x\text{-}OH]$, allowing, thus, the overall process to proceed in a catalytic way [12] (Scheme 2).

Herein, we report the results obtained with a few tetra-coordinated L_nPdCl_2 complexes [(L = 2,2′-dipyridine (dipy) (n = 1); 2-(β-diphenylphosphine)ethylpyridine) (PN) (n = 1); PPh_3 (n = 2); CH_3CN (n = 2)] which, in the presence of NEt_3·HI as co-catalyst and a mixture of CO/O_2 ($p(CO/O_2)$ = 0.1 MPa; O_2 = 5 mol%), act as environmentally benign, highly efficient and stable catalysts for the conversion α,ω-amino alcohols to *N,N′*-bis(hydroxyalkyl)ureas.

2. Experimental

2.1. General

All manipulations were carried out by using standard vacuum-line techniques. Solvents, reactants (amino alcohols, NEt_3, KI), as well as triphenylphosphine and 2,2′-bipyridine (dipy) ligands, were Aldrich or Fluka products and were used as received. PN (2-(β-diphenylphosphino)ethylpyridine) ligand and the Pd-complex $PdCl_2$(PN) were synthesized as described in the literature [13]. The other Pd(II)-complexes, $PdCl_2(PPh_3)_2$ [14], $PdCl_2$(dipy) [15] and $PdCl_2(CH_3CN)_2$ [16], were obtained according to the literature by reacting, at 343 K, a suspension of $PdCl_2$ in CH_3CN with the appropriate ligand. NEt_3·HI was prepared at 273 K, by reacting aqueous HI with an excess of NEt_3 dissolved in CH_2Cl_2. After adding the acid to the amine solution, the organic layer was separated and the salt, NEt_3·HI, was extracted from the aqueous layer with CH_2Cl_2. The CH_2Cl_2 extracts were collected together and from the resulting solution, concentrated to a small volume, white-cream crystal needles of NEt_3·HI were isolated upon addition of Et_2O.

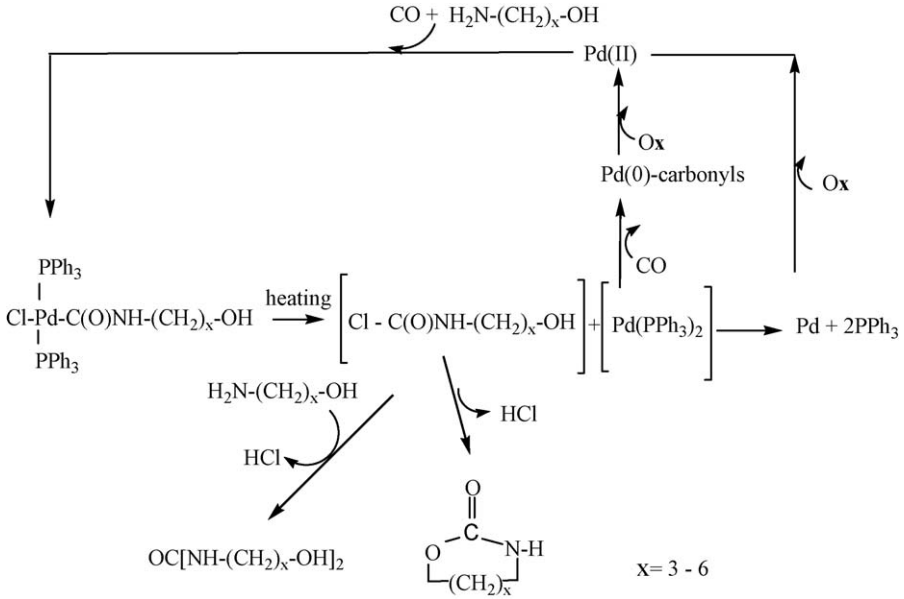
IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrophotometer. GC separations were performed by using a Varian Cromopack CP3800 GC equipped with a CP Sil 8 CB capillary column (30 m, 0.53 mm ID), connected to a FID detector. GC–MS analyses were carried out with a Shimadzu GC 17-A linked to a Shimadzu GC/MS QP5050A selective mass detector (capillary column: HP-5 MS, 30 m). NMR spectra were run on a Bruker AM 500 instrument or a Varian Inova 400 spectrometer. Gas-chromatographic analyses of gas mixtures were carried out on a Porapak Q column (3.5 m), using a Carlo Erba Fractovap GC equipped with a thermal conductivity detector.

2.2. Pd(II)-catalysed oxidative carbonylation of amino alcohols: general procedure

All reactions were carried out in a ≈100 mL glass reactor equipped with a Sovirel cap and a Thorion stopcock. Herein, as an example of typical procedure, the oxidative carbonylation of 4-aminobutanol (4-AB), catalysed by $PdCl_2$(PN)/NEt_3·HI, is described in detail.

CH_3CN (10 mL), NEt_3 (0.5 mL), 4-AB (4.00 mmol), $PdCl_2$(PN) (0.021 mmol) and NEt_3·HI (0.17 mmol; I/Pd = 8 mol/mol) were introduced into the reactor under a N_2 stream. After N_2 removal, the reactor was connected to a flask filled with a CO/O_2 mixture (O_2 = 5 mol%) at ambient pressure (761 mmHg) and temperature (300 K), introduced into an electrical oven equipped with a thermostat and a magnetic stirrer, and allowed to react at 333 K. After 7 h, the volume of consumed gas mixture was measured by means of a gas burette and the solution was analyzed for reactants and products.

The reaction mixture was reacted with pure O_2 at 333 K for 20 min (to oxidize minor amounts of Pd-black formed in the reaction system) and then cooled to room temperature. A white precipitate was obtained which was filtered off, washed with a 2:1 (v/v) Et_2O/CH_3CN mixture, dried *in vacuo* and identified as *N,N′*-bis(4-hydroxybutyl)urea by means of elemental analysis and



Scheme 2. Thermal decomposition of Pd-carbamoyl complexes from amino alcohols and formation of products under oxidative conditions.

Table 1
Oxidative carbonylation of α,ω-amino alcohols to *N,N′*-bis(hydroxyalkyl)ureas[a].

Entry	Pd-complex	Substrate	Reaction time (h)	V_{CO/O_2}[b] (mL)	Substrate consumed[c] (mmol)	Urea[d] (%)	TOF[e] (h^{-1})
1	$PdCl_2$(dipy)	3-AP	7	65 (97)	3.80 (95)	78 (82)	25.9
2	$PdCl_2$(PN)	3-AP	7	64 (95)	3.76 (94)	78 (83)	25.6
3	$PdCl_2(PPh_3)_2$	3-AP	7	62 (93)	3.72 (93)	78 (84)	25.3
4	$PdCl_2(CH_3CN)_2$	3-AP	7	55 (82)	3.24 (81)	65 (80)	22.0
5	$PdCl_2$(dipy)	4-AB	7	64 (95)	3.76 (94)	87 (93)	25.6
6	$PdCl_2$(PN)	4-AB	7	62 (92)	3.68 (90)	84 (94)	25.0
7	$PdCl_2(PPh_3)_2$	4-AB	7	80 (89)	3.52 (88)	84 (95)	23.9
8	$PdCl_2(CH_3CN)_2$	4-AB	7	54 (81)	3.16 (79)	72 (91)	21.5
9	$PdCl_2$(dipy)	5-APe	8	64 (95)	3.76 (94)	85 (90)	22.4
10	$PdCl_2$(PN)	5-APe	8	65 (97)	3.84 (96)	88 (92)	22.9
11	$PdCl_2(PPh_3)_2$	5-APe	8	62 (92)	3.60 (90)	81 (90)	21.4
12	$PdCl_2(CH_3CN)_2$	5-APe	8	56 (83)	3.28 (82)	76 (93)	19.5
13	$PdCl_2$(dipy)	6-AH	9	65 (99)	3.80 (95)	90 (95)	20.1
14	$PdCl_2$(PN)	6-AH	9	64 (95)	3.76 (94)	88 (94)	19.9
15	$PdCl_2(PPh_3)_2$	6-AH	9	60 (90)	3.52 (88)	79 (90)	18.6
16	$PdCl_2(CH_3CN)_2$	6-AH	9	50 (75)	2.96 (74)	67 (90)	15.7
18	$PdCl_2(CH_3CN)_2 + Ph_3PO$	4-AB	7	56 (81)	3.24 (81)	75 (93)	22.0

[a] Experimental conditions. Pd-complex: 0.021 mmol; substrate (amino alcohol): 4.00 mmol, NEt_3: 0.5 mL; NEt_3·HI: 0.17 mmol (I/Pd = 8 mol/mol); solvent (CH_3CN): 10 mL; CO/O_2 (19 mol/mol): 0.1 MPa; T = 333 K.
[b] Volume (mL) of gas mixture consumed. The % volume of consumed gas mixture, with respect to the stoichiometric value, is reported in parentheses.
[c] Values determined by GC. Substrate conversion (%) is reported in parentheses.
[d] Isolated yields, based on the starting material. Selectivity to urea is reported in parentheses.
[e] Mol of carbonylated substrate per mol of catalyst per hour. Based on GC yields. Error for TOF values is, in general, equal to ±0.1 h^{-1}.

Table 2
Oxidative carbonylation of 4-AB: influence of I/Pd molar ratio on the catalytic activity of $PdCl_2$(dipy)[a].

Entry	I/Pd molar ratio	V_{CO/O_2}[b] (mL)	4-AB consumed[c] (mmol)	Urea[d] (%)	TOF[e] (h^{-1})
1	0,00	Traces	Traces	Traces	–
2[f]	2	31 (47)	1.80 (45)	42 (93)	12.2
3[f]	6	58 (87)	3.44 (86)	80 (93)	23.4
4[f]	8	64 (95)	3.76 (94)	87 (93)	25.6
5[f]	10	64 (95)	3.80 (95)	87 (92)	25.9
6[g]	2	21 (31)	1.16 (29)	26 (91)	7.9
7[g]	8	44 (65)	2.56 (64)	58 (90)	17.4

[a] $PdCl_2$(dipy): 0.021 mmol; 4-AB: 4.00 mmol, NEt_3: 0.5 mL; solvent (CH_3CN): 10 mL; CO/O_2 (5 mol% O_2): 0.1 MPa; T = 333 K; reaction time: 8 h.
[b] Volume (mL) of gas mixture consumed. The % volume of consumed gas mixture, with respect to the stoichiometric value, is reported in parentheses.
[c] Values determined by GC. Substrate conversion (%) is reported in parentheses.
[d] Isolated yields, based on the starting material. Selectivity to urea is reported in parentheses.
[e] Mol of carbonylated substrate per mol of catalyst per hour. Based on GC yields. Error for TOF values is, in general, equal to ±0.1 h^{-1}.
[f] Iodide added as NEt_3·HI.
[g] Iodide added as KI.

spectroscopic techniques (IR, ^{1}H NMR, ^{13}C NMR) [12a]. The filtered mother solution, which can be directly reused for a new catalytic run (see Section 2.3 and Table 3), was analyzed by IR spectroscopy. The IR spectrum showed a weak band at 1715 cm^{-1}, assigned to cyclic carbamate 1-oxa-3-aza-cycloheptan-2-one, whose presence was also confirmed by means of GC–MS analysis of the solution (M^+ = 115 m/z) [12a].

According to the above procedure, 3-aminopropanol (3-AP), 5-aminopentanol (5-APe), 6-aminohexanol (6-AH) were also converted into the corresponding ureas, *N,N′*-bis(3-hydroxypropyl)urea, *N,N′*-bis(5-hydroxypentyl)urea and *N,N′*-bis(6-hydroxyhexyl)urea, respectively. The isolated ureas were solid compounds and were identified by means of elemental analyses and spectroscopic data. Their full characterization (IR, ^{1}H and ^{13}C NMR, MS) has been reported elsewhere [12a]. In accordance with what was found for oxidative carbonylation of 4-AB, the IR spectra of filtered reaction solutions display a weak absorption between 1722 and 1708 cm^{-1}, which, on the basis of our previous observations [12a] and GC–MS spectra, was attributed to small amounts of cyclic carbamate (1-oxa-3-aza-cyclohexan-2-one (1708 cm^{-1}; M^+ = 101 m/z), 1-oxa-3-aza-cycloctan-2-one (1722 cm^{-1}; M^+ = 129 m/z) and 1-oxa-3-aza-cyclononan-2-one (1722 cm^{-1}; M^+ = 143 m/z), respectively).

An analogous procedure was also followed when KI was used as iodide source in place of NEt_3·HI (see, for instance, entries 6 and 7, Table 2).

For further details (volume of absorbed CO/O_2 mixture, amount of reacted amino alcohol, urea yield and selectivity) see Tables 1 and 2.

2.3. Catalyst recycling

Catalyst recycling experiments were carried out using 4-AB as the substrate. After separating the urea from the reaction mixture (see also Section 2.2), fresh 4-AB (4.00 mmol) was added to the filtered mother solution. The resulting mixture was allowed to

Table 3
Catalyst recycling: TOF[a] (h^{-1}) values over six cycles[b].

Catalyst	Cycles					
	1st	2nd	3rd	4th	5th	6th
$PdCl_2$(dipy)	25.6	25.2	24.6	24.0	23.7	23.5[c]
$PdCl_2$PN	25.0	24.5	24.2	23.9	23.5	23.8[c]
$PdCl_2(PPh_3)_2$	23.9	23.7	23.5	23.3	23.1	23.4[d]
$PdCl_2(CH_3CN)_2$	21.5	16.3	8.5	4.9		

[a] Mol of carbonylated substrate per mol of catalyst per hour. Based on GC yields. Error for TOF values is, in general, equal to ±0.1 h^{-1}.
[b] 4-AB (4.00 mmol) was used as the amino alcohol, in all the runs. See also Section 2.3.
[c] 0.021 mmol of ligand were added in this run.
[d] 0.042 mmol of ligand were added in this run.

react with CO/O_2 for 7 h at 333 K and then treated as described in Section 2.2. The TOF values observed in each recycling experiment have been reported in Table 3.

2.4. Elucidation of the catalytic steps

2.4.1. Reductive step: stoichiometric reaction of $PdCl_2(PPh_3)_2$ with 4-AB and CO

To a suspension of $PdCl_2(PPh_3)_2$ (0.600 g, 0.86 mmol) in CH_3CN (10 mL), both NEt_3 (0.5 mL) and 4-AB (0.170 g, 1.89 mmol; 4-AB/Pd = 2.2 mol/mol) were added under a N_2 stream. N_2 was pumped off and CO was introduced at atmospheric pressure into the glass reactor. The mixture was allowed to react at room temperature for 24 h. In the long run the suspension, initially yellow, turned white-cream and, then, pink. The IR spectrum of the reaction solution (orange) showed bands at 1858 (w) and 1834 (w, br) cm^{-1}, respectively assigned to the three-nuclear carbonyl complexes $Pd_3(CO)_3(PPh_3)_3$ and $Pd_3(CO)_3(PPh_3)_4$ [17]. The reaction mixture was filtered and the pink residue was characterized as a mixture of $Pd_3(CO)_3(PPh_3)_3$ and *N,N′*-bis(4-hydroxybutyl)urea. The separation of the latter compounds was easily achieved by treating the mixture with methanol, which readily dissolved the urea. The red residue, insoluble in methanol, was identified as $Pd_3(CO)_3(PPh_3)_3$ (0.238 g; yield based on palladium: 70%). IR(nujol): (νCO), 1860 cm^{-1} [17]. Elemental analysis. Calcd for $C_{57}H_{45}O_3P_3Pd_3$ (%): C, 57.52; H, 3.81; P, 7.81; Pd, 26.83. Found: C, 57.46; H, 3.97; P, 7.76; Pd, 26.74.

The methanol solution was evaporated *in vacuo*. From the residue, after washing with toluene to remove residual traces of Pd(0)-carbonyls, a white solid was isolated, whose IR spectrum was identical to that of a pure sample of *N,N′*-bis(4-hydroxybutyl)urea (0.52 mmol). More urea (0.15 mmol) was recovered from the CH_3CN mother solution (see above) by evaporating *in vacuo* the solvent and washing the white residue with toluene and, then, diethyl ether (urea overall yield: 78%).

2.4.2. Oxidative step

$Pd_3(CO)_3(PPh_3)_3$, isolated as reported above (see Section 2.4.1), was allowed to react with O_2, for 6 h, under various conditions (see, below, items (i)–(iii)).

(i) $Pd_3(CO)_3(PPh_3)_3$ was added to the filtered CH_3CN solution ensuing from the oxidative step (see Section 2.4.1) and reacted with O_2 either in the absence (run (*a*)) or in the presence of added triphenylphosphine (run (*b*): added PPh_3/Pd = 1 mol/mol);

(ii) $Pd_3(CO)_3(PPh_3)_3$ was added to a CH_3CN solution of NEt_3·HCl (Cl/Pd = 2.3) and reacted with O_2 in the presence of added PPh_3 (run (*c*): added PPh_3/Pd = 1 mol/mol; run (*d*): added PPh_3/Pd = 1.5 mol/mol);

(iii) $Pd_3(CO)_3(PPh_3)_3$ was added to a CH_3CN solution of NEt_3·HI (I/Pd = 2.3) and reacted with O_2 in the presence of added PPh_3 (run (*e*): added PPh_3/Pd = 1 mol/mol; run (*f*): added PPh_3/Pd = 1.5 mol/mol).

In all the runs ((*a*)–(*f*)), to minimize the decomposition of the Pd(0)-complex to Pd-black, reaction temperature was gradually increased to 333 K during the first 2 h, and then maintained constant at this value for the remaining time.

Runs (*a*)–(*d*): The colour of the reaction solution, initially orange, turned yellow very slowly (∼3–4 h). *trans*-$PdCl_2(PPh_3)_2$, impure of Pd-metal, was isolated by filtration. Pure $PdCl_2(PPh_3)_2$ was obtained by extraction with hot CH_2Cl_2 and identified by means of elemental analysis and the IR spectrum, which were similar to those of an authentic sample. Elemental analysis. Calcd for $C_{36}H_{30}Cl_2P_2Pd$ (%): Cl, 10.10; P, 8.82; Pd, 15.16. Found: Cl, 10.06; P, 8.78; Pd, 15.11. *trans*-$PdCl_2(PPh_3)_2$ yield: 50–60%. The best yields were obtained in the experiments using an excess of phosphine.

Runs (*e*) and (*f*): The colour of the reaction solution, initially orange, turned red-brown very rapidly (30 min). In this case, pure $PdI_2(PPh_3)_2$, identified by means of IR spectroscopy and elemental analysis, was isolated. Elemental analysis. Calcd for $C_{36}H_{30}I_2P_2Pd$ (%): I, 28.68; P, 7.00; Pd, 12.03. Found: I, 28.61; P, 6.94; Pd, 11.98; Cl, traces. *trans*-$PdI_2(PPh_3)_2$ yield: 90–95%. The best yields were obtained in the experiments using an excess of phosphine.

In all the runs ((*a*)–(*f*)), the GC analysis of the reaction solution showed the formation of variable amounts of triphenylphosphine oxide.

3. Results and discussion

3.1. Oxidative carbonylation of α,ω-amino alcohols promoted by L_nPdCl_2/NEt_3·HI systems: factors affecting the catalytic activity

Under safe and very mild conditions (303–333 K; $p(CO/O_2)$ = 0.1 MPa; O_2 = 5 mol%), L_nPdCl_2/NEt_3·HI systems [(L = 2,2′-dipyridine (dipy) (*n* = 1); 2-(β-diphenylphosphine)ethylpyridine) (PN) (*n* = 1); PPh_3 (*n* = 2); CH_3CN (*n* = 2)] effectively promote the oxidative carbonylation of α,ω-amino alcohols, as 3-AP, 4-AB, 5-APe and 6-AH, to the corresponding *N,N′*-bis(hydroxyalkyl)ureas (Eq. (1)) with high yield and selectivity (Tables 1 and 2). All the urea products were isolated as crystalline solids and characterized by means of IR and NMR spectroscopy [12a].

$$2H_2N\text{-}(CH_2)_x\text{-}OH + CO + 1/2O_2 \rightarrow OC[NH\text{-}(CH_2)_x\text{-}OH]_2 + H_2O \quad (x = 3\text{–}6) \qquad (1)$$

The catalytic process was monitored by means of GC and IR analysis of reaction solution and by measuring the volume of gas mixture consumed. As CO_2 was never found among the reaction products, the volume of gas consumed can be related directly with the amount of amino alcohol carbonylated. Table 1 shows the results obtained when the amino alcohols 3-AP, 4-AB, 5-APe and 6-AH were reacted with CO/O_2 mixtures (0.1 MPa; O_2 = 5 mol%) in the presence of the catalytic systems L_nPdCl_2/NEt_3·HI, at 333 K and using a I/Pd molar ratio equal to 8. Under the working conditions (Table 1), good to excellent substrate conversions (74–96%) and urea yields (67–90%, isolated) were achieved within reasonable times (7–9 h) with all the amino alcohols, whatever L_nPdCl_2 (L = = dipy, PN, PPh_3, CH_3CN) catalyst was used. Selectivity to urea (based on isolated product) was excellent (≥90%) for amino alcohols 4-AB, 5-APe and 6-AH. A lower, but still satisfactory, selectivity (80–84%) was found for the carbonylation of 3-AP to *N,N′*-bis(3-hydroxypropyl)urea because of more significant side-formation, in this case, of the six-membered cyclic carbamate 1-oxa-3-aza-cyclohexan-2-one. The latter fact can find an easy rationale in the shorter aliphatic chain, which makes the –OH and –NH_2 functional groups closer in 3-AP than in the other substrates, a structural feature expected to facilitate, in the case of 3-AP, the cyclization side-process affording the cyclic carbamate.

A greater insight into the catalytic process comes from the inspection of the TOF (turnover frequency) values reported in Table 1, which allow to compare not only the efficiency of a given catalytic system in the carbonylation of the different substrates, but also their different activities in the ureidization of a given amino alcohol. The TOF values (Table 1) show that, whatever substrate (3-AP, 4-AB, 5-APe and 6-AH) was used, the catalytic activity was affected by the nature of the ancillary ligand coordinated to palladium and decreased in the order: dipy ≈ PN > PPh_3. In the absence of any ligand, a less efficient catalytic system was obtained (see Table 1, entries 4, 8, 12, 16).

Moreover, whatever $L_nPdCl_2/NEt_3{\cdot}HI$ [(L = 2,2′-dipyridine (dipy) (n = 1); 2-(β-diphenylphosphine)ethylpyridine) (PN) (n = 1); PPh_3 (n = 2); CH_3CN (n = 2)] system was utilized, the TOF values decreased in the order 3-AP > 4-AB > 5-APe > 6-AH (Table 1), showing that the longer the amino alcohol aliphatic chain, the lower the rate of carbonylation process.

The influence of other factors, such as the I/Pd molar ratio, as well as the nature of iodide source, was also investigated, using 4-AB as reference substrate and $PdCl_2$(dipy) as the Pd-catalyst (Table 2). The results reported in Table 2 show unambiguously that (a) iodide has a beneficial effect on the catalytic activity (see also Section 3.2.2) and (b) the catalytic efficiency (TOFs) markedly depends on the I/Pd molar ratio. In the absence of any iodide source, substrate conversion was negligible and only trace amounts of urea were formed (entry 1, Table 2). Using $NEt_3{\cdot}HI$ as iodide source, a marked increase of TOF was observed for I/Pd values rising between 0 and 8 mol/mol (entries 2–4, Table 2). I/Pd molar ratios higher than 8 bring about only a very modest increase of TOF (entry 5, Table 2). A different iodide promoter, such as KI, was also effective, but not as efficient as $NEt_3{\cdot}HI$ (entries 6 and 7, Table 2). KI/Pd molar ratios up to 10 have been employed in Pd-catalysed oxidative carbonylation of vicinal amino alcohols under relatively mild conditions [2c].

The catalytic systems investigated are stable under the working conditions and can be easily recovered and reused for successive runs. Recovery of the catalytic system can be accomplished in a direct simple way. At the end of the catalytic run the reaction mixture was allowed to react for about 20 min with pure O_2, to avoid loss of Pd-catalyst as Pd-metal. Urea was separated by filtration and the filtered solution was reusable for a new catalytic run (see Section 2.3). Catalyst recycling experiments (Table 3) were carried out using, in each run, fresh 4-AB as substrate, which was reacted with a CO/O_2 mixture (0.1 MPa; O_2 = 5 mol%) at 333 K for 7 h. The TOF (h^{-1}) values measured for the different Pd-catalysts over several (up to six) recycling runs are reported in Table 3. The catalytic activity decayed steadily when $PdCl_2(CH_3CN)_2$ was used as catalyst, a behaviour which finds full rationalization in the reaction mechanism discussed in the next section (see Section 3.2.2). When the catalytic activity of metal centre (Pd) was assisted by ancillary ligands as dipy, PN or PPh_3, TOF diminished very slowly after each run. In these cases the slight decrease of catalytic efficiency over successive cycles can be ascribed to unavoidable minor losses of catalyst during the recovery procedure and, with the catalytic systems stabilized by PPh_3 or PN, to the oxidation of the ligands.[1] Accordingly, the TOF values measured for the sixth recycling (Table 3) show that, upon adding free ligand to the catalyst solutions deriving from the fifth cycle, the catalytic activity increased only for the catalytic systems stabilized by P- or P,N-donor ligands as PPh_3 or PN.

3.2. Reaction mechanism and catalytic cycle

It is well established [18] that transition metal promoted oxidative carbonylation of alcohols or amines proceeds generally through two basic steps. In the first step, carbonylation of substrate is accompanied by reduction of the metal centre, whose oxidation state decreases by two units (Eq. (2)). In the second step, the metal centre is reoxidized (Eq. (3)) by the used oxidant. The starting catalytic species is thus regenerated and can initiate a new catalytic cycle.

$$L_nM^{(+n)} + CO + 2HY \rightarrow COY_2 + L_nM^{+(n-2)} + 2H^+ \quad (Y = OR;\ NHR) \qquad (2)$$

[1] Table 1 shows clearly that the catalytic system based on phosphine oxide $OPPh_3$ is also effective (entry 18), but less efficient than the system based on PPh_3 (entry 7).

$$L_nM^{+(n-2)} + 2H^+ + 1/2O_2 \rightarrow L_nM^{(+n)} + H_2O \qquad (3)$$

We were also able to ascertain that the carbonylation of amino alcohol to urea (Eq. (1)) promoted by palladium(II)-complexes may proceed through such a mechanism. Herein, we discuss a few major mechanistic features of the overall catalytic process.

3.2.1. The reductive step

To get a greater insight into the reductive step, $PdCl_2(PPh_3)_2$ and 4-AB were reacted stoichiometrically under a CO atmosphere (0.1 MPa) in the presence of an excess of tertiary amine (NEt_3), at room temperature (Eq. (4)). The reaction afforded the corresponding urea, *N,N′*-bis(4-hydroxybutyl)urea, together with the polynuclear "$Pd(PPh_3)$-carbonyl" complexes $Pd_3(CO)_3(PPh_3)_3$ and $Pd_3(CO)_3(PPh_3)_4$, detected in the reaction solution by means of IR analysis (bands at 1858 and 1838 cm^{-1}, respectively) [17]. Only *N,N′*-bis(4-hydroxybuthyl)urea and $Pd_3(CO)_3(PPh_3)$ precipitated from the reaction medium and were isolated as pure compounds in 78% and 70% yields, respectively.

$$PdCl_2(PPh_3)_2 + CO + 2H_2N\text{-}(CH_2)_4\text{-}OH + 2NEt_3 \rightarrow OC[NH\text{-}(CH_2)_4\text{-}OH]_2 + \text{"}Pd(PPh_3)\text{-carbonyl"} + 2NEt_3{\cdot}HCl \qquad (4)$$

The hydroxyalkylurea formed also when $PdCl_2(CH_3CN)_2$ was used in place of $PdCl_2(PPh_3)_2$, showing that the nature of the ancillary ligand does not affect markedly the course of the carbonylation step. Nevertheless, the data in Table 3 demonstrate that the ancillary ligand can play a crucial role in stabilizing the catalytically active species and prolonging the lifetime of the catalytic system.

We have ascertained that the reductive carbonylation step involves, as the key intermediate, a relatively unstable carbamoyl complex $L_nPdCl[C(O)NH\text{-}(CH_2)_x\text{-}OH]$, which forms according to reaction (5). Nevertheless, the PPh_3-complexes are fairly stable and have been isolated recently by us, fully characterized by means of IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy and studied for their reactivity [12a]. Upon heating, $L_nPdCl[C(O)NH\text{-}(CH_2)_x\text{-}OH]$ complexes can decompose by generating the corresponding cyclic carbamate. However, when heated in the presence of an excess of the amino alcohol (and, therefore, under conditions closer to those used in the catalytic process) the corresponding urea $OC[NH\text{-}(CH_2)_x\text{-}OH]_2$ was formed (Scheme 2).

$$L_nPdCl_2 + CO + 2H_2N\text{-}(CH_2)_x\text{-}OH + NEt_3 \rightarrow L_nPdCl[C(O)NH\text{-}(CH_2)_x\text{-}OH] + NEt_3{\cdot}HCl \qquad (5)$$

3.2.2. The oxidative step

To achieve a better understanding of the oxidative step and the factors affecting it, the complex $Pd_3(CO)_3(PPh_3)_3$ was separated from the urea and reacted with O_2 under various conditions (see Section 2.4.2).

In a few experiments, $Pd_3(CO)_3(PPh_3)_3$ was re-combined with the mother liquor (see Section 2.4.2) and the resulting mixture was reacted with O_2 either in the absence or in the presence of added phosphine (reaction (6); see Section 2.4.2, runs (*a*) and (*b*)). In other related experiments, $Pd_3(CO)_3(PPh_3)_3$ was suspended in a CH_3CN solution of $NEt_3{\cdot}HCl$ and reacted with O_2, in the presence of PPh_3 (reaction (7); added $PPh_3/Pd \geq 1$ mol/mol; see also Section 2.4.2, runs (*c*) and (*d*)). In all the cases, reoxidation of Pd(0) (reactions (6) and (7)) was very slow at room temperature. At higher temperatures (313–333 K) it was relatively faster, but, after 6 h,

afforded $PdCl_2(PPh_3)_2$ in moderate

$$Pd_3(CO)_3(PPh_3)_3 \xrightarrow{\text{mother liquor}(PPh_3+NEt_3HCl),O_2} PdCl_2(PPh_3)_2 + \text{products} \quad (6)$$

$$Pd_3(CO)_3(PPh_3)_3 + 6NEt_3HCl + 3PPh_3 \xrightarrow{O_2} 3PdCl_2(PPh_3)_2 + \text{products} \quad (7)$$

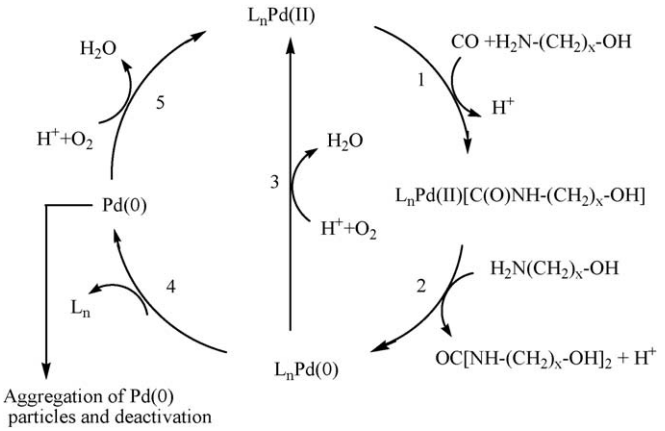
yield (max 60%, isolated) as the complex $Pd_3(CO)_3(PPh_3)_3$ partially decomposed to Pd-metal, which was hardly oxidized to Pd(II) under the working conditions.

Prompt reoxidation of Pd(0)-species to Pd(II) is a factor of crucial importance for the lifetime of the catalytic system and efficiency (TOF) of the catalytic process and can be facilitated by using a suitable oxidation promoter able to speed up the reoxidation reaction. To this end, stoichiometric amounts of expensive oxidants as $Cu(OAc)_2$ have been used [2e], which has been shown to be effective under relatively mild conditions. Other authors focused on the use of iodide as co-catalyst, but the catalytic systems investigated so far were effective only under relatively more drastic conditions [2c,19]. In the present study we have shown that the use of NEt_3·HI as iodide source co-catalyst promotes easy reoxidation of Pd(0) to Pd(II) by dioxygen and allows the overall process to proceed effectively, under very mild conditions. Accordingly, $Pd_3(CO)_3(PPh_3)_3$ readily converted into $PdI_2(PPh_3)_2$ (90–95% isolated yield) when reacted with O_2 in the presence of NEt_3·HI and phosphine (see Section 2.4.2 runs (*e*) and (*f*)). Also reoxidation of Pd-metal (Eq. (8)) took place more easily in the presence of the iodide salt and ligand. Reoxidation of Pd-black, which can occur also in the absence of any ligand [2c,19] is of particular relevance to catalysis, as it allows to individuate an additional pathway through which, under catalytic conditions (313–333 K; $p(CO/O_2)$ = 0.1 MPa), the catalycally active species can be regenerated.

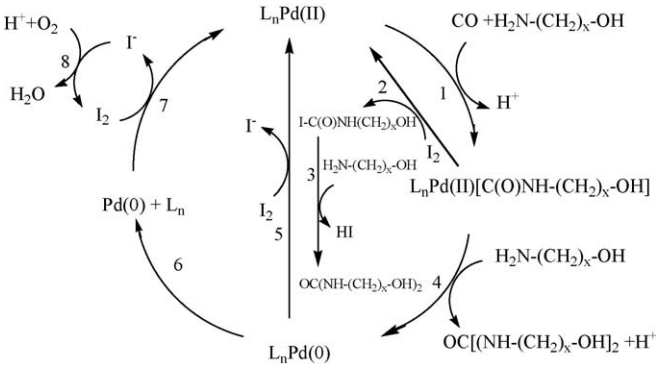
$$Pd(0) + 2PPh_3 + 1/2O_2 + 2NEt_3HCl \rightarrow PdCl_2(PPh_3)_2 + H_2O + 2NEt_3 \quad (8)$$

For instance, when reaction (4) was carried out at 333 K, palladium black formed during the reductive step (Eq. (4)) was rapidly oxidized in quantitative yield only if NEt_3·HI was added to the system before the reaction mixture reacted with O_2. In the absence of NEt_3·HI the reoxidation reaction was slower and incomplete after a reaction time of 6 h. Moreover, if the mixture resulting from the reductive step (Eq. (4)) was stirred for about 2 h under N_2 before being reacted with O_2, Pd-black formed during the process became much more reluctant to oxidation, even in the presence of NEt_3·HI. This fact may be ascribed to the tendency of colloidal palladium formed during the reaction to undergo a passivation process, which likely involves aggregation of nanoparticles of the metal. Such a phenomenon is well described in the literature, and it is known that some palladium based catalytic systems, in which the active species are colloidal metal particles, exhibit enhanced activity in the presence of protective agents, as polyvinylalcohols or surfactants, able to protect palladium metal particles against aggregation [20].

Scheme 3 summarizes the behaviour of the reacting system in the absence of the iodide promoter. Under the latter conditions, catalysis is poor as decomposition of Pd(0)-complexes takes place faster than the reoxidation process, which is slow in the absence of NEt_3·HI. The consequent increase of concentration of metal nanoparticles in the reaction medium facilitates their aggregation and causes the fast deactivation of catalytic system. In the presence of NEt_3·HI (Scheme 4) the oxidative step is faster. This fact maintains the concentration of metal nanoparticles at low levels,



Scheme 3. Catalytic cycle in the absence of iodide promoters.



Scheme 4. Catalytic cycle in the presence of NEt_3.HI.

to prevent aggregation of Pd particles and deactivation of catalytic system.

In general, all those factors able to stabilize Pd(0)-species prolong the lifetime of catalytic system and prevent its deactivation to Pd-metal. In this regard, we note that a substantial improvement of efficiency of the overall catalytic process results from employing N- or P-donor ancillary ligands (dipy, PN, PPh_3), which, by stabilizing low-valent Pd(0)-complexes, can restrain their deactivation to less easily reoxidable Pd-metal or, also, assist the reoxidation of Pd nanoparticles to Pd(II), as described in Eq. (8). This may explain why the systems based on L_nPdCl_2 complexes (L = dipy, PN, PPh_3) were more effective than those based on $PdCl_2(CH_3CN)_2$ (Tables 1 and 3).

As is well documented in the literature [2c,8,9,19,21], in the presence of iodide, dioxygen is not directly involved in reoxidation of palladium, but the latter step implies the direct reaction of Pd(0)-complexes or black palladium with molecular iodine (Eqs. (9) and (10)), which generates *in situ* by oxidation of iodide with O_2 (Eq. (11)). Reaction (11) requires a source of protons. The influence of acidity on oxidation of iodide provides an easy rationale for the fact that, under our conditions, NEt_3·HI is a more efficient co-catalyst than KI (compare, in Table 2, entries 2 and 4 with entries 6 and 7, respectively). In fact, differently from KI, which can behave only as iodide source, NEt_3·HI may also act as proton donor, making the protons required for iodide oxidation more easily available in the reaction medium.

$$L_nPd + I_2 \rightarrow L_nPd(II) + 2I^- \quad (9)$$

$$Pd(0) + L_n + I_2 \rightarrow L_nPd(II) + 2I^- \quad (10)$$

$$2I^- + 2H^+ + 1/2O_2 \rightarrow I_2 + H_2O \quad (11)$$

Although the data reported above individuate in the discussed mechanism a very plausible reaction pathway, we also note that iodine formed in the reaction mixture may open an additional way to the formation of the target product and the regeneration of the Pd(II)-catalyst (Scheme 4 routes 2–3). Elsewhere [11,12], in fact, we have demonstrated that iodine can easily react with Pd-carbamoyl complexes. This reaction can regenerate the starting Pd-catalyst and afford a reactive carbamoyl iodide (Eq. (12)), which can be converted into urea by reaction *in situ* with the substrate (Eq. (13)).

$$Pd(PPh_3)_2Cl[C(O)NH\text{-}(CH_2)_x\text{-}OH] + I_2 \rightarrow Pd(PPh_3)_2Cl(I) + IC(O)NH\text{-}(CH_2)_x\text{-}OH \quad (12)$$

$$IC(O)NH\text{-}(CH_2)_x\text{-}OH + H_2N\text{-}(CH_2)_x\text{-}OH \rightarrow OC(NH\text{-}(CH_2)_x\text{-}OH)_2 + HI \quad (13)$$

4. Conclusions

α,ω-Amino alcohols have been effectively and selectively carbonylated, in CH_3CN, to symmetrical *N,N′*-bis(hydroxyalkyl)ureas using Pd(II)/L/NEt_3/HI (L = dipy, PN, PPh_3, CH_3CN) catalytic systems and molecular oxygen as the oxidant. Using NEt_3·HI as co-catalyst acting both as iodide source and proton donor formation of urea proceeds efficiently under very mild conditions (303–333 K; $p(CO/O_2)$ = 0.1 MPa). The iodide source, as well as the nature of ancillary ligands, is of crucial importance for lifetime of catalytic system and the efficiency of the catalytic process. The best catalytic activities were observed using Pd-systems stabilized by mono- or bidentate N- or P-donor ligands and employing an I/Pd molar ratio close to 8.

The urea can be isolated in a very straightforward way and the catalytic system can be easily recovered and recycled for several times without showing any significant decrease in activity (L = dipy, PN, PPh_3).

A few mechanistic features of the process have also been investigated. Formation of urea involves the intermediacy of $L_nPdCl[C(O)NH\text{-}(CH_2)_x\text{-}OH]$ carbamoyl complexes. This step can also generate Pd(0)-species, which are easily reoxidized to Pd(II) in the presence of NEt_3·HI and O_2.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2009.12.022.

References

[1] (a) M.R. Barbachyn, C.W. Ford, Angew. Chem. Int. Ed. 42 (2003) 2010–2013;
(b) C.M. Perry, B. Javis, Drugs 61 (2001) 525–551;
(c) R. Norrby, Exp. Opin. Pharmacother. 2 (2001) 293–302;
(d) D. Clemmet, A. Markhan, Drugs 59 (2000) 815–827;
(e) T.A. Muktar, G.D. Wright, Chem. Rev. 105 (2005) 529–542;
(f) J.M. Cassady, K.K. Chan, E.G. Floss, E. Leistner, Chem. Pharm. Bull. 52 (2004) 1–26.
[2] (a) F.W. Li, X.G. Peng, C.G. Xia, B. Hu, Chin. J. Chem. 23 (2005) 643–645;
(b) I. Chiarotto, M. Feroci, Tetrahedron Lett. 42 (2001) 3451–3453;
(c) B. Gabriele, R. Mancuso, G. Salerno, M. Costa, J. Org. Chem. 68 (2003) 601–604;
(d) B. Gabriele, G. Salerno, D. Brindisi, M. Costa, G.P. Chiusoli, Org. Lett. 2 (2000) 625–627;
(e) K. Orito, M. Miyazawa, T. Nakamura, A. Horibata, H. Ushito, H. Nagasaki, M. Yuguchi, S. Yamashita, T. Yamazaki, M. Tokuda, J. Org. Chem. 71 (2006) 5951–5958.
[3] (a) F.W. Li, C.G. Xia, J. Catal. 227 (2004) 542–546;
(b) J.M. Liu, X.G. Peng, J.H. Liu, S.Z. Zheng, W. Sun, C.G. Xia, Tetrahedron Lett. 48 (2007) 929–932.
[4] (a) N.A. Puschin, R.V. Mitic, Justus Liebigs Ann. Chem. 532 (1937) 300–303;
(b) A.F. Hegarty, L.J. Drenman, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), Comprehensive Organic Functional Group Transformation, vol. 6, Pergamon, Oxford, UK, 1998, pp. 499–526;
(c) T.P. Vishnyavova, I.A. Golubeva, E.V. Glebova, Russ. Chem. Rev. (Engl. Transl.) 54 (1985) 249–261;
(d) J.E. McClusker, A.D. Main, K.S. Johnson, C.A. Grasso, L. McElwee-White, J. Org. Chem. 65 (2000) 5216–5222.
[5] M.K. Leung, J.L. Lai, K.H. Lau, H.H. Yu, H.J. Hsiao, J. Org. Chem. 61 (1996) 4175–4179.
[6] (a) J.R. Gage, D.A. Evan, Org. Synth. 68 (1990) 77–82;
(b) D.J. Ager, I. Prakash, D.R. Schaad, Chem. Rev. 96 (1996) 835–875 (and references therein);
(c) M. Feroci, A. Gennaro, A. Inesi, M. Orsini, L. Palombi, Tetrahedron Lett. 43 (2002) 5863–5865.
[7] D.J. Diaz, K.G. Hylton, L. McElwee-White, J. Org. Chem. 71 (2006) 734–738.
[8] P. Giannoccaro, C.F. Nobile, M. Latronico, Inorg. Chim. Acta 175 (1990) 133–139.
[9] (a) P. Giannoccaro, N. Ravasio, M. Aresta, J. Organomet. Chem. 451 (1993) 243–248;
(b) P. Giannoccaro, J. Organomet. Chem. 470 (1994) 249–252.
[10] P. Giannoccaro, D. Cornacchia, S. Doronzo, E. Mesto, E. Quaranta, M. Aresta, Organometallics 25 (2006) 2872–2879.
[11] (a) P. Giannoccaro, I. Tommasi, M. Aresta, J. Organomet. Chem. 476 (1994) 13–18;
(b) M. Aresta, P. Giannoccaro, I. Tommasi, Educ. Adv. Chem. 3 (1996) 249–255;
(c) M. Aresta, P. Giannoccaro, I. Tommasi, A. Dibenedetto, A.M. Manotti, F. Ugozzoli, Organometallics 19 (2000) 3879–3889.
[12] (a) P. Giannoccaro, A. Dibenedetto, M. Gargano, E. Quaranta, M. Aresta, Organometallics 27 (2008) 967–975;
(b) P. Giannoccaro, S. Doronzo, M. Gargano, P. Masiello, E. Quaranta, M. Aresta, Europacat VIII, 26–31 August, 2007, Turku-Finland, pp. 5–30.
[13] E. Uhlig, Z. Keiser, Anorg. Chem. 406 (1974) 1–6.
[14] J. Chatt, L.H. Venanzi, J. Chem. Soc. (1957) 2351–2355.
[15] B.J. McCormick, E.N. Jaynes Jr., R.I. Caplan, H.C. Clarck, J.D. Ruddick, Inorg. Synth. 13 (1971) 216–218.
[16] B.B. Wayland, R.F. Schramm, Inorg. Chem. 8 (1969) 971–976.
[17] M. Hidai, M. Kokura, Y. Ochida, J. Organomet. Chem. 52 (1973) 431–435.
[18] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Carbonylation: Direct Synthesis of Carbonyl Compounds, Plenum Press, New York, 1991 (Chapter 2, p. 30).
[19] (a) B. Gabriele, M. Costa, G. Salerno, G. Chiusoli, J. Chem. Soc., Perkin Trans. 1 (1994) 83–87;
(b) B. Gabriele, G. Salerno, in: D. Crich (Ed.), PdI2 in e-EROS (Electronic Encyclopedia of Reagents for Organic Synthesis), Wiley-Interscience, 2006, pp. 1–13;
(c) B. Gabriele, M. Costa, G. Salerno, G. Chiusoli, Curr. Org. Chem. 8 (2004) 919;
(d) B. Gabriele, M. Costa, G. Salerno, Synlett 14 (2004) 2468–2483;
(e) B. Gabriele, G. Salerno, Top. Organomet. Chem. 18 (2006) 239–272;
(f) B. Gabriele, G. Salerno, M. Costa, G.P. Chiusoli, J. Organomet. Chem. 687 (2003) 219–228;
(g) B. Gabriele, R. Mancuso, G. Salerno, M. Costa, Chem. Commun. 4 (2003) 486–487;
(h) B. Gabriele, G. Salerno, R. Mancuso, M. Costa, J. Org. Chem. 69 (2004) 4741–4750;
(i) D.J. Díaz, A.K. Darko, L. McElwee-White, Eur. J. Org. Chem. 27 (2007) 4453–4465.
[20] (a) X. Sun, X. Jiang, S. Dong, E. Wang, Macromol. Rapid Commun. 24 (2003) 1024–1028;
(b) T. Douglas, M. Young, Nature 393 (1998) 152–155;
(c) F.C. Meldrum, B.R. Heywood, S. Mann, Science 257 (1992) 522–523;
(d) S.-H. Yu, M. Antonietti, H. Cölfen, M. Giersig, Angew. Chem. Int. Ed. Engl. 41 (2002) 2356–2359;
(e) L.I. Halaoui, Langmuir 17 (2001) 7130–7136;
(f) Q.F. Zhou, J.C. Bao, Z. Xu, J. Mater. Chem. 12 (2002) 384–387;
(g) L. Longenberger, G. Mills, J. Phys. Chem. 99 (1995) 475–478;
(h) S. Mann, J.P. Hannington, R.J.P. Williams, Nature 324 (1986) 565–567;
(i) M.P. Peleni, J. Tanori, A. Felakembo, J.C. Dedieu, T. Gulik-Krzywicki, Langmuir 14 (1998) 7359–7363.
[21] (a) P. Giannoccaro, M. Aresta, S. Doronzo, C. Ferragina, Appl. Organomet. Chem. 14 (2000) 581–589;
(b) P. Giannoccaro, S. Doronzo, C. Ferragina, in: H.U. Blaser, A. Baiker, R. Prins (Eds.), Homogeneous Catalysis and Fine Chemicals IV, Elsevier Science B.V., 1997, pp. 633–640.