



Recent developments in the synthesis of heterocyclic derivatives by PdI₂-catalyzed oxidative carbonylation reactions

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Dedicated to Professor J.P. Genêt in recognition of his significant contributions to the art of organic synthesis, on the occasion of his 60th birthday

Abstract

A simple catalytic system, consisting of PdI₂ in conjunction with an excess of KI, has proven to be very valuable for the direct one-step synthesis of a variety of heterocyclic derivatives by oxidative carbonylation of suitably functionalized alkynes. The same catalyst also promoted the oxidative carbonylation of β-amino alcohols to oxazolidin-2-ones with unprecedented catalytic efficiencies for this kind of reaction.

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1. Introduction

Pd-catalyzed oxidative carbonylation reaction is a very important methodology for the direct synthesis of carbonyl compounds starting from readily available starting materials [1]. During the last decade, there has been considerable research activity in this field, mainly devoted to the study of new catalytic systems able to promote new synthetic transformations as well as to catalyze already known processes but with a higher selectivity and efficiency.

In this account, we will review our recent achievements in the synthesis of a variety of functionalized heterocyclic compounds by oxidative cyclocarbonylation–alkoxycarbonylation, cyclization–alkoxycarbonylation, or cyclocarbonylation reactions, starting from suitably functionalized alkynes or β-amino alcohols. We will show that a very simple

catalytic system, consisting of PdI₂ in conjunction with an excess of KI, has proven to be very active and versatile for the achievement of new carbonylative processes leading to heterocycles.

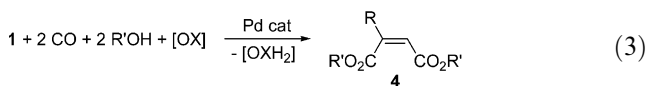
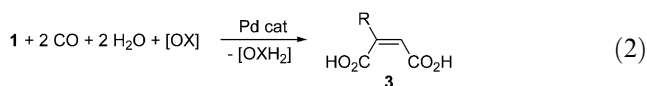
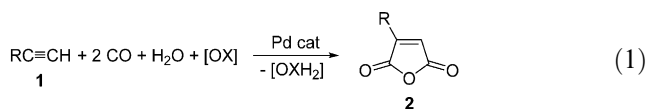
The emphasis of this short review will be on synthetic applications of our methodology rather than on mechanistic aspects. All the elementary steps involved in the proposed mechanistic pathways are well known in organopalladium chemistry [1,2], and are discussed to some extent, also with reference to literature precedents for model reactions, within our original papers cited in the reference list.

2. Background: oxidative dicarbonylation of alk-1-ynes

Palladium-catalyzed oxidative dicarbonylation of alk-1-ynes **1** in the presence of a nucleophilic species is a well-known process, which, depending on the nature and the amount of nucleophile and reaction conditions, leads to maleic anhydrides **2** (Eq. (1)), maleic acids **3** (Eq. (2)) or maleic diesters **4** (Eq. (3)).

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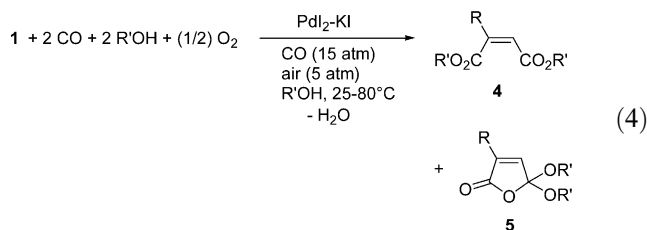
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The first catalysts employed for performing these reactions were based on PdCl₂, in the presence of different ligands or additives. Thus, many years ago acetylene was converted into dimethyl maleate using catalytic amounts of PdCl₂ in the presence of two equivalents of thiourea as ligand at room temperature and under an atmospheric pressure of a 24.5:68:7.5 mixture of acetylene:CO:air in MeOH as the solvent (Eq. (3), R = H, [OX] = (1/2)O₂, [OXH₂] = H₂O) [3]. A catalytic efficiency of about 60 mol of product per mol of PdCl₂ was obtained. Subsequently, maleic diesters were obtained in high yields from simple alk-1-yne using PdCl₂ as catalyst in the presence of CuCl₂ as co-catalyst under acidic conditions (HCl) and under a CO/O₂ atmosphere in alcoholic media (Eq. (3), [OX] = (1/2)O₂, [OXH₂] = H₂O); catalytic efficiencies not higher than 25 mol of product per mol of PdCl₂ were however achieved [4]. The same catalytic system under similar conditions was employed for the synthesis of maleic anhydrides **2** (30–75% yield, catalytic efficiencies up to 7.5 mol of **2** per mol of Pd) in THF–HCO₂H–H₂O [5]. More recently, **2** were obtained in fair yields using PdCl₂ as catalyst and CuCl₂ as oxidizing agent in water/dioxane (Eq. (1), [OX] = 2CuCl₂, [OXH₂] = 2 CuCl + 2 HCl) [6]; halide-free catalytic systems have also been reported, both homogeneous [7] and heterogeneous [8]. In all these processes, however, the catalytic efficiencies obtained were usually only moderate (up to ca. 100 mol of **2** per mol of Pd used with R = Ph, lower with R = alkyl).

We have recently shown that PdI₂ in conjunction with a tenfold excess of KI is a superior catalyst for the oxidative dicarbonylation of alk-1-yne, allowing, under appropriate conditions, the selective preparation of all maleic derivatives **2**, **3** or **4** in high selectivity and with excellent catalytic efficiencies (up to ca. 4000 mol of product per mol of Pd used). Maleic diesters **4** were obtained in high yields by working in alcoholic solvents at 25–80 °C and under 20 atm of a 3:1 mixture of carbon monoxide and air, 5,5-dialkoxyfuran-2(5*H*)-ones (**5**) being also formed as by-products (Eq. (4)) [9]. These compounds, which can be regarded as cyclic isomers of maleic diesters, readily converted into **4** by

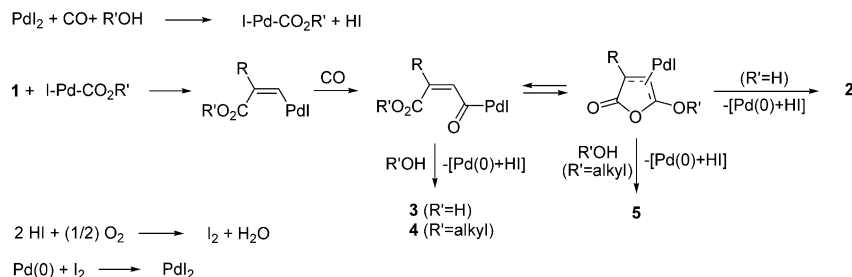
working at higher temperatures or by acid-catalyzed alcoholysis. An elegant application of this reaction has been recently reported in the key steps of the synthesis of the carbocyclic core of phomoidride **B** (CP-263,114) [10]. Under similar conditions (80 °C under 20 atm of a 4:1 mixture CO:air) but in a 3:1 mixture of 1,2-dimethoxyethane (DME)–H₂O as the solvent, maleic acids were obtained selectively [11]. Finally, maleic anhydrides **2** were formed in good yields by working in dioxane in the presence of a slight excess of H₂O with respect to **1** [11]. Interestingly, in this latter case saturation of the reaction mixture with an excess of CO₂ (CO₂:CO:air = 40:16:4 atm) was necessary in order to obtain satisfactory selectivities.



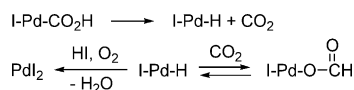
R	R'	Yield of 4 (%)	Yield of 5 (%)
H	Me	89	
Bu	Me	67	13
Bu	Bu	55	14
Ph	Me	46	37
Ph	H	71	
CH ₂ OH	Me	77	13
CH ₂ OAc	Me	56	34

We believe that a fast reoxidation of Pd(0) ensuing from the oxidative carbonylation process is responsible for the high catalyst activity. In fact, Pd(0) reoxidation under our conditions occurs through oxidative addition by I₂, formed by oxidation with O₂ of HI, also ensuing from the oxidative carbonylation process (Scheme 1; anionic iodide ligands are omitted for clarity).

The striking effect exerted by CO₂ in the reaction leading to anhydrides **2** is related to the fact that, in the presence of a large excess of carbon dioxide, the concentration of H–Pd–I species (in equilibrium with Pd(0)+HI or formed by decarboxylation of the I–Pd–CO₂H species), relatively stable in an aprotic low-polar solvent such as dioxane and responsible for side processes, is lowered through the reversible formation of a palladium–formate complex, as shown in Scheme 2 [11].



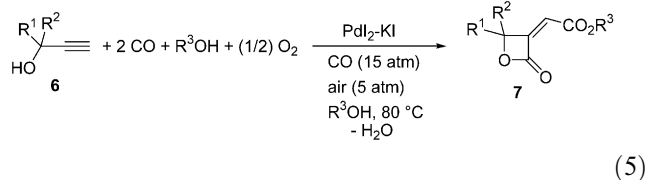
Scheme 1.



Scheme 2.

3. Synthesis of heterocycles by PdI₂-catalyzed oxidative cyclocarbonylation–alkoxycarbonylation of functionalized alkynes

The application of our PdI₂-based oxidative carbonylation methodology to propynyl alcohols led to very interesting results. Thus, while the reaction of simple prop-2-yn-1-ol and but-3-yn-2-ol under the usual conditions (PdI₂+10 KI as catalyst, *P*(CO)=15 atm, *P*(air)=5 atm, *T*=80 °C) selectively led to the corresponding maleic diesters, (*Z*)- α -(alkoxycarbonyl)methylene- β -lactones (**7**) were formed as the main products (41–80% yield, catalytic efficiencies up to 1080 mol of **7** per mol of Pd used) starting from α,α -dialkylsubstituted propynyl alcohols or 4-ethylhex-1-yn-3-ol **6** (Eq. (5)) [12].



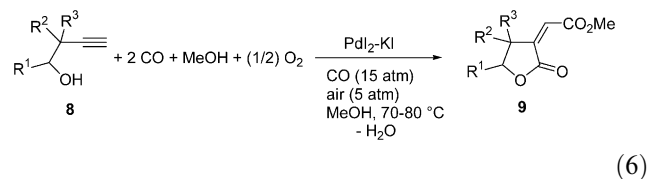
(5)

R ¹	R ²	R ³	Yield of 7 (%)
Me	Me	Me	80
Me	Me	Bu	44
Et	Me	Me	76
(CH ₂) ₅		Me	57
CHEt ₂	H	Me	52

This result was particularly significant from a synthetic point of view, since it was the first time that propynyl alcohol could be converted into β -lactones by a Pd-catalyzed carbonylation reaction. Moreover, the fact that cyclization occurred only in the presence of α,α -dialkyl substitution or α -monoalkyl substitution with a bulky group, gave insight into the reaction

mechanism. In fact, the steric effect exerted by the substituents causes the inversion of the regiochemistry of insertion of the I–Pd–CO₂R³ species into the triple bond with respect to simple alk-1-ynes, thus allowing, after CO insertion, intramolecular nucleophilic attack by the –OH group (Scheme 3). The presence of a single α -methyl group is clearly not sufficient to cause this regiochemical inversion, as shown by the results obtained with but-3-yn-2-ol.

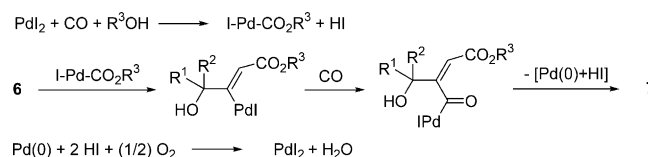
The reaction was extended to the synthesis of (*Z*)- α -(methoxycarbonyl)methylene- γ -lactones (**9**) starting from 3-yn-1-ols (**8**) (Eq. (6)) [12b]. Interestingly, the presence of α -substitution was not required in this case for cyclization to occur. This suggests a different mechanism, which starts from the formation of an alkoxycarbonyl species from the alcoholic function of the substrate. This intermediate, stabilized by coordination of the triple bond, undergoes triple bond insertion followed by alkoxycarbonylation (Scheme 4).



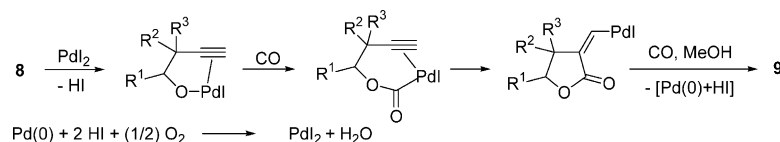
(6)

R ¹	R ²	R ³	Yield of 9 (%)
H	H	H	86
Me	H	H	94
H	Me	Me	73
	(CH ₂) ₃ (<i>cis</i>)	H	93

Propynyl amines turned out to be much less reactive than propynyl alcohols under the usual conditions. This is probably due to the basicity of the substrates, which

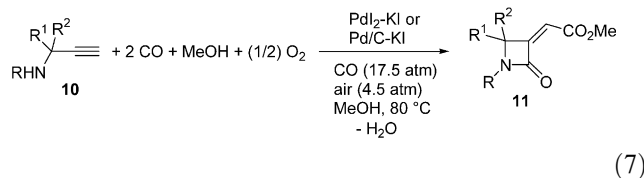


Scheme 3.



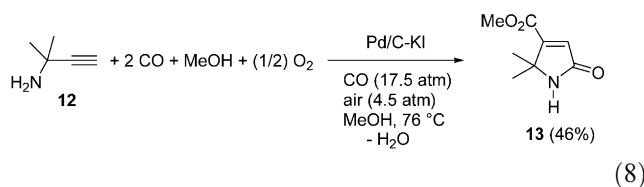
Scheme 4.

lowers the concentration of HI in solution thus hampering the Pd(0) reoxidation. The carbonylation reaction occurred only when the substrate to catalyst molar ratio was lowered to 30–50 [13]. Pd/C–KI could also be used in place of PdI₂–KI in these reactions, the active species PdI₄²⁻ being formed in situ by Pd(0) oxidation under the reaction conditions. As expected, (*Z*)- α -(methoxycarbonyl)methylene- β -lactams (**11**) were obtained in moderate to good yields (35–80%) starting from *N*-substituted α,α -dialkyl substituted propynyl amines (**10**) (Eq. (7)).

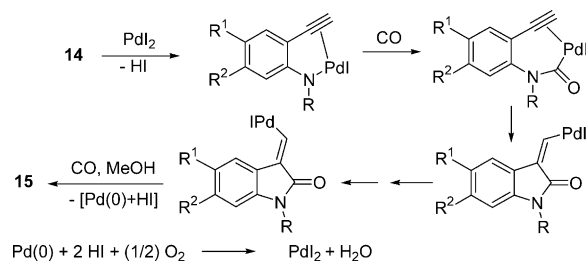


R	R ¹	R ²	Yield of 11 (%)
Bn	Me	Me	71
Bn	Et	Me	80
Bu	Me	Me	35
Allyl	Me	Me	40

Quite interestingly, however, 1,1-dimethylprop-2-ynylamine (**12**), bearing a primary amino group, followed a different reaction course leading to γ -lactam derivative **13** as the main product (46% yield, Eq. (8)). Double bond isomerization at the vinylpalladium intermediate level [14] can be responsible for γ -lactone formation (Scheme 5).

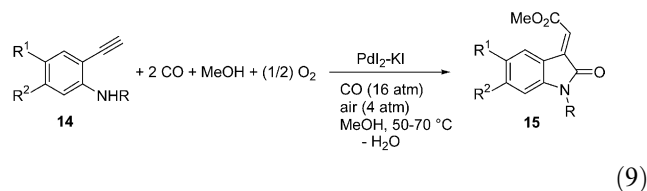


A similar double bond isomerization also occurred in the case of carbonylation of 2-ethynylanilines (**14**), which afforded (*E*)-3-(methoxycarbonyl)methylene-1,3-



Scheme 6.

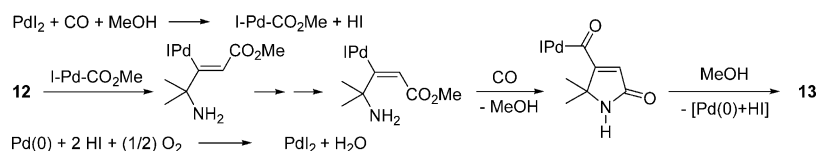
dihydroindol-2-ones (**15**) selectively (Eq. (9) and Scheme 6) [15].



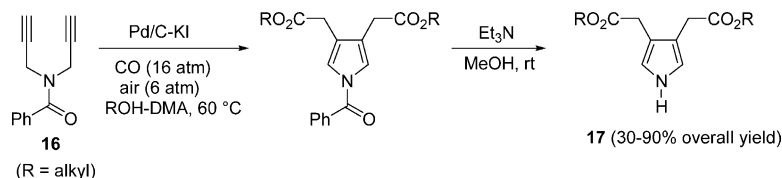
R	R ¹	R ²	Yield of 15 (%)
H	H	H	60
Bn	H	H	55
H	Me	H	64
H	Cl	H	56
H	H	Cl	48

4. Synthesis of heterocycles by PdI₂-catalyzed oxidative cyclization–alkoxycarbonylation of functionalized alkynes

The application of our oxidative carbonylation methodology to suitably functionalized 1,5-diynes has permitted a facile synthesis of new pyrrole and thiophenic derivatives. Thus, *N,N*-diprop-2-ynylbenzamide (**16**) could be converted into 3,4-bis[(alkoxycarbonyl)methyl]pyrroles (**17**) in moderate to high yields



Scheme 5.



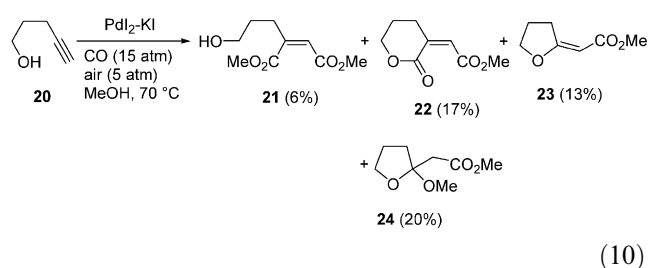
Scheme 7.

(30–90%) according to Scheme 7 [16]. The initially formed 1-benzoyl-3,4-bis(methoxycarbonyl)methylene]tetrahydropyrroles were isomerized into the corresponding pyrroles under basic conditions, either in a separate step with Et_3N [16a] or in situ with *N,N*-dimethylacetamide as co-solvent [16b]. These pyrrole derivatives have been used for the preparation of new porphyrins with mesogenic properties [16b].

Analogously, 3,4-bis[(methoxycarbonyl)methyl]thiophene (**19**) was easily prepared from carbonylation of diprop-2-ynyl sulfide (**18**) to give 3,4-bis[(methoxycarbonyl)methylene]tetrahydrothiophene followed by base-catalyzed aromatization (40% overall yield, Scheme 8) [17]. This thiophene derivative has been employed as building block for the synthesis of novel oligothiophenic materials, which have found application in the construction of new LED devices [18] and in the synthesis of new erbium-substituted oligothiophene chelates for infrared emission [19].

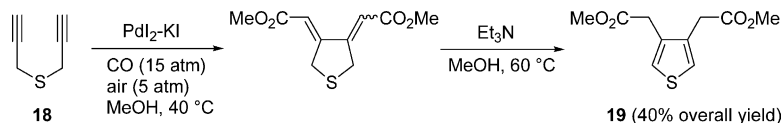
In both cases, the carbonylation reaction occurs through triple bond insertion into the $\text{I-Pd-CO}_2\text{R}$ species followed by ring closure through insertion of the second triple bond, and alkoxy carbonylation of the resulting vinylpalladium intermediate (Scheme 9).

The reaction of pent-4-yn-1-ol (**20**) carried out under conditions similar to those employed for 3-yn-1-ols (**8**) (see Eq. (6)) led to a mixture of dicarbonylated products **21** and **22** (23% total yield) and monocarbonylated products **23** and **24** (33% total yield, Eq. (10)) [20]. Product **24** derived from MeOH addition to the vinyl ether bond of **23**, and readily converted into **23** by bulb-to-bulb distillation of the reaction crude under reduced pressure.

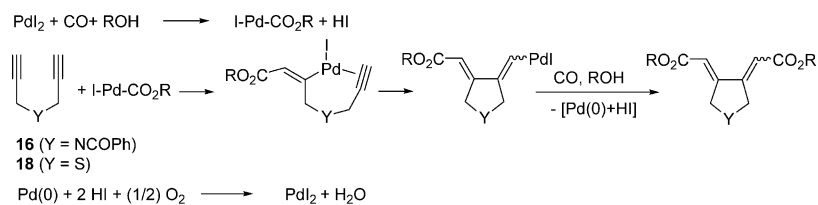


While products **21** and **22** were formed through reaction patterns similar to those shown in Schemes 1 and 4, respectively, product **23** corresponded to a completely different reaction pattern, i.e. *anti* 5-*exo-dig* intramolecular nucleophilic attack of the $-\text{OH}$ group on triple bond coordinated to Pd(II) followed by stereospecific methoxycarbonylation (Scheme 10). As we have seen, neither propynyl alcohols **6** nor 3-yn-1-ols **8** showed this latter kind of reactivity. With **6** and **8**, according to Baldwin's rules [21], an *exo* attack was unfavorable for stereoelectronic reasons, while an *endo* attack, although stereoelectronically possible, was not observed.

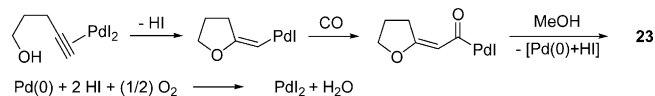
Quite interestingly, the reaction could be effectively directed towards the formation of monocarbonylated products **23** and **24** (64% total yield) by working at higher CO pressure (100 atm of a 9:1 mixture of CO and air). We interpreted this result as follows. In the presence of an excess of CO ligand, the insertion of the triple bond into the $\text{Pd-CO}_2\text{Me}$ bond, which is a necessary step for the formation of dicarbonylated products, is effectively slowed down. On the other hand, a higher carbon monoxide pressure tends to favor the CO insertion into the vinylpalladium intermediate leading to **23**. Under these conditions, other 4-yn-1-ols



Scheme 8.

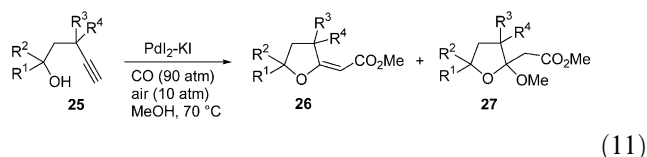


Scheme 9.



Scheme 10.

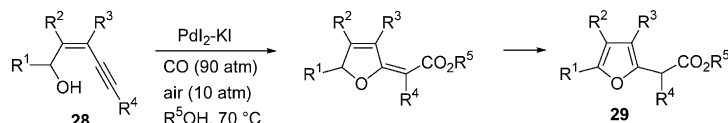
25 afforded the corresponding tetrahydrofuran derivatives **26**+**27** in good yields and excellent catalytic efficiencies (up to ca. 2300 mol per mol of PdI₂, Eq. (11)). Analogously to **24**, compounds **27** readily converted into **26** by bulb-to-bulb distillation of the reaction crude under reduced pressure.



R ¹	R ²	R ³	R ⁴	Yield of 26 (%)	Yield of 27 (%)
H	H	H	H	24	40
Me	H	H	H	32	45
Me	Me	H	H	41	37
H	H	Me	Me	56 ^a	19

^aIncluding the *Z* isomer (29%).

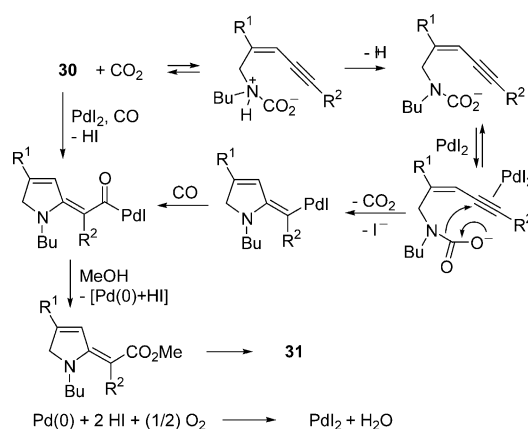
A particularly important application of this kind of reactivity was obtained with (*Z*)-2-en-4-yn-1-ols (**28**). In this case, in fact, the initially formed (*E*)-2-[(alkoxycarbonyl)methylene]-2,5-dihydrofurans (which in some cases have been isolated) underwent spontaneous or acid-catalyzed aromatization to give furan-2-acetic esters (**29**) in high yields and catalytic efficiencies (Scheme 11) [22].



Scheme 11.

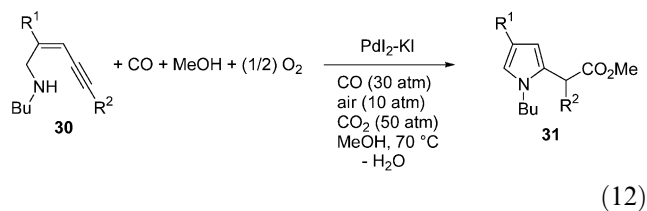
R ¹	R ²	R ³	R ⁴	R ⁵	Yield of 29 (%)
H	H	Me	H	Me	82
H	H	Me	H	Bu	51
H	H	Ph	H	Me	62
H	H	Me	Ph	Me	73
H	H	H	Bu	Me	59
H	Ph	H	Bu	Me	80
Et	Et	H	Bu	Me	65

The analogous reaction of (*Z*)-(2-en-4-ynyl)amines (**30**), carried out under similar conditions, afforded the corresponding pyrrole-2-acetic esters (**31**) in low yields, since the substrates preferentially underwent oxidative degradation and/or oligomerization rather than carbonylation. This result is again ascribable to the basicity of **30**, which hinders the reoxidation of Pd(0). However, we have found that by buffering the basicity of **30** with an excess of CO₂ (50 atm), the oxidative carbonylation process may effectively take place with formation of **31** in good yields (Eq. (12)) [23]. In fact, while CO₂ is able to lower the basicity of the amino group through the formation of a carbamate species, it does not hinder the carbonylation process leading to **31**, since CO₂ may be



Scheme 12.

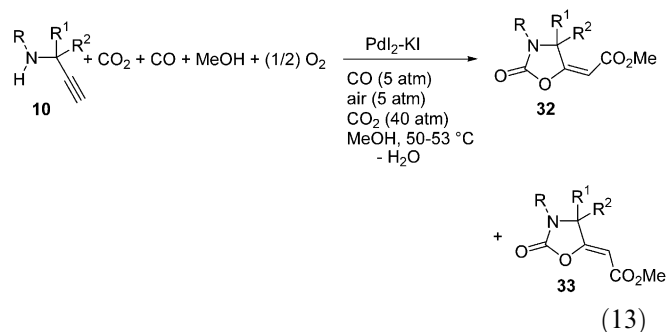
eliminated during the cyclization process (Scheme 12). This reaction represents the first example in which carbon dioxide has been shown to act as a promoter in an oxidative carbonylation process.



R ¹	R ²	Yield of 31 (%)
Et	Bu	70
Ph	Bu	65
Et	TMS	72 ^a

^a R² = H in the final product.

When the oxidative carbonylation of α,α -dialkyl *N*-alkyl substituted propynyl amines **10** was carried out in the presence of added CO₂ (40 atm), the intermediate carbamate species formed in situ was already geometrically and stereoelectronically suitable to give direct attack to the triple bond without need of losing CO₂. Thus, under these conditions, **10** were selectively converted into new stereoisomeric oxazolidin-2-one derivatives **32** and **33** (Eq. (13)) [24]. β -Lactams (**11**), selectively obtained in the reaction carried out in the absence of added CO₂ (see Eq. (7)), were formed only in traces in this case. This reaction represents the first example of catalytic carboxylation-carbonylation of an organic substrate.

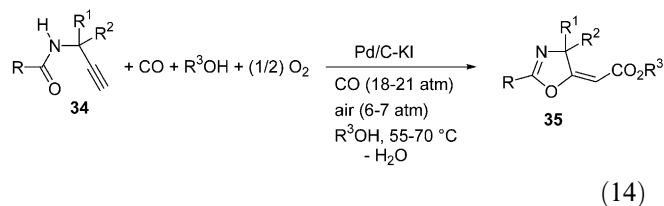


R	R ¹	R ²	Yield of 32 (%)	Yield of 33 (%)
Bu	Me	Me	21	62
Bn	Me	Me	30	59

It is worth noting that products **32** and **33** did not interconvert under the reaction conditions. Therefore, they originate from different reaction pathways, either

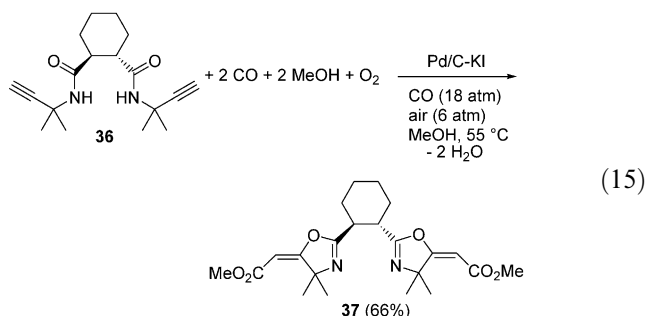
anti 5-*exo-dig* attack of the free carbamate anion to the triple bond or *syn* addition to the triple bond of a palladium carbamate species (Scheme 13).

Anti 5-*exo-dig* cyclization, resulting from attack by the oxygen of the amide function to the triple bond coordinated to Pd(II), followed by methoxycarbonylation also occurred in the case of α,α -dialkyl prop-2-ynylamides (**34**), with formation in high yields of new oxazoline derivatives **35** (Eq. (14) and Scheme 14) [13,25].

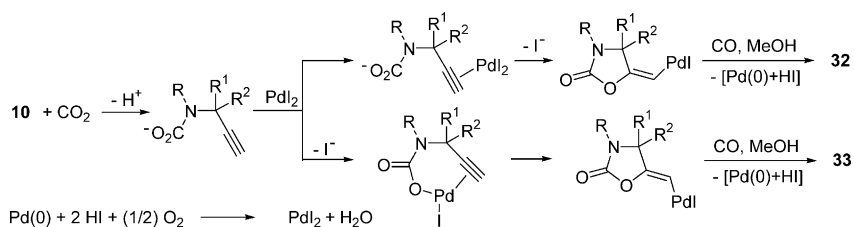


R	R ¹	R ²	R ³	Yield of 35 (%)
Me	Me	Me	Me	65
Ph	Me	Me	Me	83
CH=CH ₂	Me	Me	Me	57
CH=CHCO ₂ Et	Me	Me	Et	84
2-pyridyl	Me	Me	Me	83

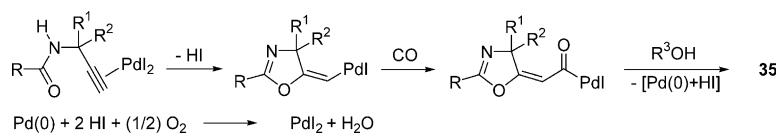
The reaction has been successfully extended to the synthesis of bisoxazolines (51–69% yield) starting from acetylenic diamides, as exemplified by the formation of bisoxazoline (**37**) from the bis-[(1,1-dimethylprop-2-ynyl)amide] of *trans*-cyclohexane-1,2-dicarboxylic acid (**36**) (Eq. (15)) [25].



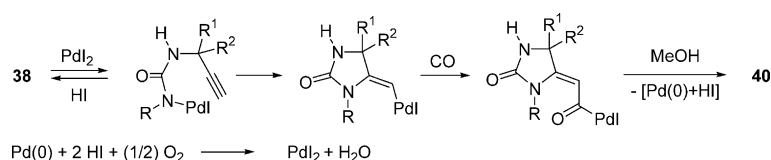
Interestingly, propynyl ureas **38** under similar conditions afforded two types of products simultaneously: oxazolines **39–39'** and cyclic ureas **40** containing (*E*)- or (*Z*)-(methoxycarbonyl)methylene chains, respectively, depending on whether the cyclization was initiated by oxygen or nitrogen attack on the triple bond (Eq. (16)) [26].



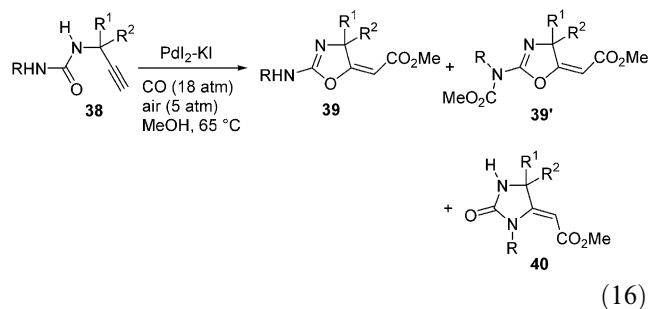
Scheme 13.



Scheme 14.



Scheme 15.



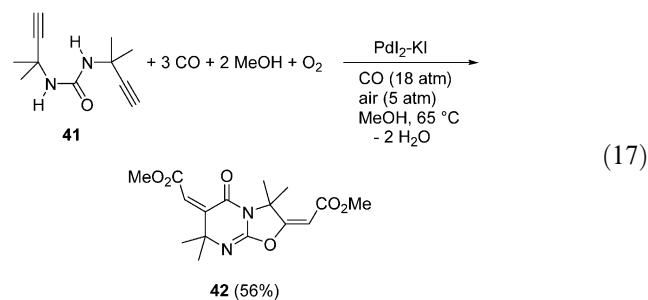
(16)

R	R ¹	R ²	Yield of 39 (%)	Yield of 39' (%)	Yield of 40 (%)
Pr	Me	Me	70	3	23
Bn	Me	Me	33		53
Ph	Me	Me	34	33	7
<i>p</i> -MeC ₆ H ₄	Me	Me	47		35
H	Me	Me		28	46

Formation of **40** may be interpreted as occurring through *syn* insertion of the triple bond into the N–Pd bond resulting from the reaction between PdI₂ and the –NHR moiety of the urea, followed by carbon monoxide insertion and nucleophilic displacement by MeOH (Scheme 15).

A remarkable double cyclization reaction was observed in the oxidative carbonylation of diacetylenic ureas, as exemplified in Eq. (17) for the conversion of **41**

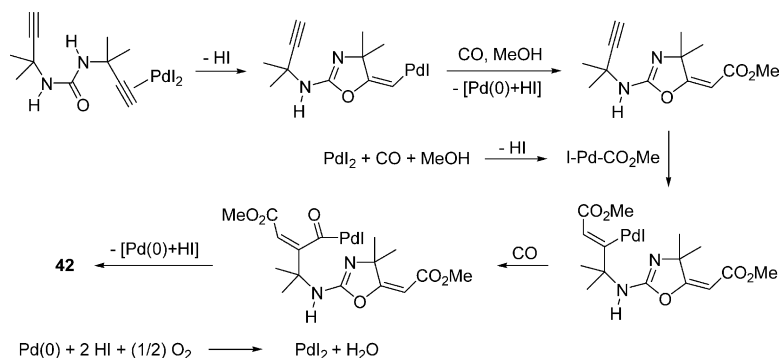
into a 2,3,6,7-tetrahydrooxazolo[3,2-*a*]pyrimidin-5-one derivative **42** [26]. In this case, in fact, the initially formed oxazolinone intermediate undergoes *syn* insertion of the I–Pd–CO₂Me species into the second triple bond, followed by CO insertion and intramolecular nucleophilic attack by the nitrogen of the oxazolinone ring to the resulting acylpalladium intermediate (Scheme 16).



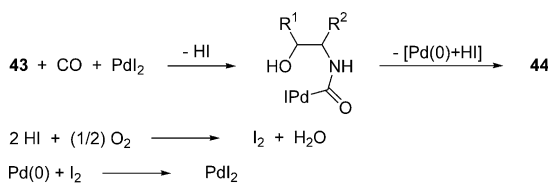
(17)

5. Synthesis of oxazolidin-2-ones by PdI₂-catalyzed oxidative cyclocarbonylation of β-amino alcohols

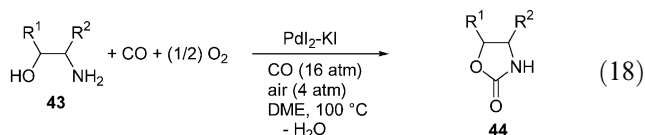
The PdI₂-KI catalytic system also proved useful for performing the oxidative carbonylation of β-amino alcohols **43** to give oxazolidin-2-ones **44** in excellent yields (90–100%) and with unprecedented catalytic efficiencies for this kind of reaction (up to 2000 mol of product per mol of Pd, Eq. (18) and Scheme 17) [27].



Scheme 16.



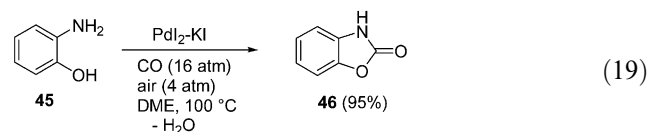
Scheme 17.



R ¹	R ²	Yield of 44 (%)
H	H	96
Me	H	96
Ph	H	93
H	Me	100
H	Ph	97
H	Me ₂ CH	94
H	PhCH ₂	90

Initially, carbonylations were carried out in MeOH as the solvent, and, in order to compensate for the basicity of the substrate in this solvent, a large excess of oxygen (partial pressure 35 atm) and of KI (KI–PdI₂ molar ratio = 200) were employed [27a]. In fact, in the presence of a large excess of I[−], the acid–base equilibrium between the substrate and HI (necessary, as usual, for Pd(0) reoxidation) may be partially shifted to the left. Moreover, a high O₂ partial pressure may further favor the oxidation of HI to I₂, thus allowing fast regeneration of the catalytically active species PdI₂. Later, however, it was found that, by just changing the reaction solvent from MeOH to 1,2-dimethoxyethane (DME), the carbonylation could be carried out under only 1 atm of O₂ and ten equivalents of KI with respect to PdI₂, i.e. under conditions similar to those employed for alk-1-ynes [27b]. This is clearly connected with the lower basicity

of the substrate in this latter solvent, which is aprotic and low-polar, but sufficiently coordinating to allow dissolution of the PdI₂–KI catalytic system. Moreover, the possibility to accomplish the reaction under milder oxidizing conditions has permitted the application of the methodology to 2-aminophenol (**45**), which under the original conditions in MeOH underwent a competitive oxidative dimerization process: in DME under 1 atm of O₂, this substrate was converted into benzoxazolin-2-one (**46**) in excellent yield and with catalytic efficiencies as high as 4750 mol of **46** per mol of Pd used (Eq. (19)) [27b].



6. Conclusions

Summing up, the PdI₂–KI catalytic system has proven to be a very versatile and effective catalyst for performing the oxidative cyclocarbonylation–alkoxycarbonylation, cyclization–alkoxycarbonylation, or cyclocarbonylation of different functionalized alkynes, β-amino alcohols and 2-aminophenol leading to a variety of interesting heterocyclic derivatives. The catalyst is particularly attractive in view of its simplicity and its ability to achieve high turnover numbers in most cases. This latter characteristic, together with the fact that it works in association with oxygen as the oxidizing agent (and thus with formation of water as co-product), makes the PdI₂–KI catalyst also very valuable from the standpoint of atom economy.

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