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Combined oxidative and reductive carbonylation of terminal alkynes with palladium iodide–thiourea catalysts

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Abstract

Oxidative carbonylation of alkynes can be carried out catalytically in the absence of added oxidants if it is coupled with a reductive carbonylation process at the expense of the same alkyne involved in the oxidative process. Maleic esters (from oxidative carbonylation) and unsaturated lactones (from reductive carbonylation) are the main products formed under the catalytic action of palladium iodide complexes with thiourea (tu). A complex, formally corresponding to the ionic formula $[PdI(tu)_3]I$, allows the reaction of alkylacetylenes at room temperature and atmospheric pressure. With activated alkynes such as phenylacetylene, or with alkynes containing coordinating groups, other palladium complexes with two or four molecules of thiourea are also active, although to a lesser extent. Identification of the organic by-products gives a hint of the mechanism by which coupling of oxidative and reductive carbonylation occurs.

Keywords: Palladium; Alkynes; Oxidative carbonylation; Reductive carbonylation; Catalysis; Thiourea

1. Introduction

Some time ago we reported [1a] that the combination of stoichiometric oxidative carbonylation of phenylacetylene or of some coordinating alkynes with reductive carbonylation at room temperature and atmospheric pressure of carbon monoxide, under the catalytic action of $[Pd(tu)_4]Cl_2$ (tu = thiourea), leads to an additive carbonylation process (Eq. 1, R′ = alkyl).

Reaction 1 gave a 1 : 1 ratio of maleic ester to lactone. Intermolecular reactions in which oxidative carbonylation was combined with a reduction process have also been reported [1b,c]. Although thiourea proved to be the most efficient ligand for carbonylation under mild conditions, extension to dialkylacetylenes failed and alkylacetylenes gave poor results. This prompted us to study the catalytic system in more detail.

2. Results and discussion

We found that PdI_2 was more effective than $PdCl_2$ and that the thiourea/Pd molar ratio was critical. $[Pd(tu)_2I_2]$ and $[Pd(tu)_4]I_2$ were prepared and both were found to be poor catalysts for the carbonylation of alkynes. The former readily produced palladium black, while the latter reacted very slowly. When we used a PdI_2–thiourea system with a thiourea/Pd ratio of 3 and, even better, 3.5, we found that the reaction proceeded readily to give good conversions and yields.

In a typical procedure, the alkyne, 2.78 mmol in 7 ml of methanol, was caused to react with carbon monoxide at 25°C and atmospheric pressure in the presence of 0.139 mmol of PdI_2 + 0.486 mmol of thiourea. With hex-1-yne the reaction was complete after 8 h and gave a 94% yield of products, which were separated by column chromatography. Products and yields for this and other substrates are reported in Table 1.

The oxidative carbonylation products (**1** + **2** + **3**) are approximately equal to those coming from reductive carbonylation (**4** + **5**). Slight differences are due to partial reduction of the palladium complex. Products **6**, **7** and **8** correspond to additive carbonylation, according to Eqs. 2 and 3.

$$RC{\equiv}CH + CO + MeOH \xrightarrow{Pd(cat)} \mathbf{6} + \mathbf{7} \qquad (2)$$

$$RC{\equiv}CH + 2CO + 2MeOH \xrightarrow{Pd(cat)} \mathbf{8} \qquad (3)$$

Products **5a** and **5′c** formally correspond to further reduction of the double bond of an unsaturated aldehyde

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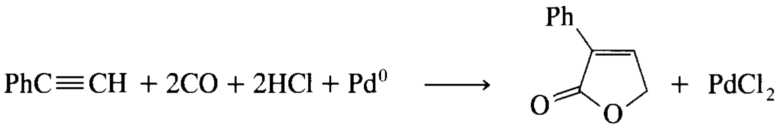
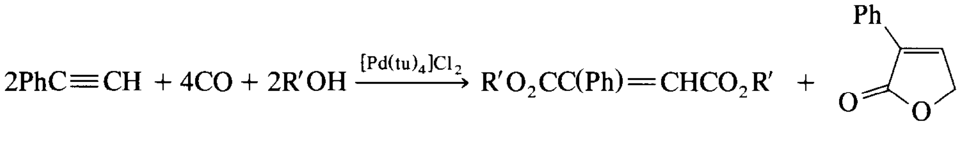
$$\mathrm{PhC{\equiv}CH + 2CO + 2R'OH + PdCl_2 \longrightarrow R'O_2CC(Ph){=}CHCO_2R' + 2HCl + Pd(0)}$$





(1)

followed by acetalization. Product **3b**, obtained from phenylacetylene, is the cyclic tautomer of **1b** [2]. As shown in Table 1, when the reaction was carried out with $[Pd(tu)_4]I_2$ and hex-1-yne no reaction occurred, whereas with $[Pd(tu)_2I_2]$ the total yield was only 56% after 24 h. With $[Pd(tu)_3I]I$ an 82% yield was obtained in 8 h. The addition of 0.5 mol of thiourea in excess brought the yield to 94%. The excess is probably needed to compensate partial thiourea dissociation due to the acid present in solution. This is confirmed by the fact that when a coordinating group was present in the alkyne, as in the case of $HC{\equiv}C(CH_2)_3CN$, the best results were obtained with 3 mol of thiourea per mole of Pd, ca. 90% yield being reached in 24 h, with a product distribution similar to that observed with hex-1-yne. With PhC≡CH the complex containing three molecules of thiourea gave a 98% yield in 5 h. Phenylacetylene coordinates to palladium much better than alkylacetylenes and the reaction can also be performed with thiourea/palladium ratios below 3, although the reaction rates are lower.

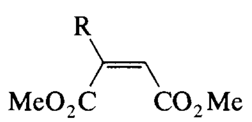
To obtain information on the nature of the palladium iodide–thiourea catalysts, we determined their molecular weights in methanol by vapour pressure osmometry and their conductivities in methanol.

$[Pd(tu)_4]I_2$ has a molecular weight of 240–245 (at 52°C), which is higher than expected (222 because the X-ray structure shows that the complex is ionic in the solid state [3]), suggesting the presence in solution of a less dissociated species such as $[Pd(tu)_4I]I$ (MW332). This is confirmed by the conductivity ($\lambda = 133.9$ ohm^{-1} cm^2 mol^{-1} at 10^{-3} mol l^{-1}), which is greater than the upper limit for a 1 : 1 electrolyte (80–115) and less than the lowest value for a 2 : 1 electrolyte (160–220) [4a].

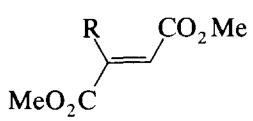
$[Pd(tu)_4](BF_4)_2$ was prepared for comparison. The molecular weight at 52°C was found to be 192–197 (calc. 195) and λ was 195.1 ohm^{-1} cm^2 mol^{-1} at 10^{-3} mol l^{-1}, as expected for a 1 : 2 electrolyte.

$[Pd(tu)_2I_2]$ has a molecular weight of 320–340 at 45°C, which reveals a limited degree of dissociation (calc. 256 for $[Pd(tu)_2I]I$ and 512 for $[Pd(tu)_2I_2]$, neglecting possible solvent association). The conductivity ($\lambda = 50.3$ ohm^{-1} cm^2 mol^{-1} at 10^{-3} mol l^{-1}) is lower than that of a 1 : 1 electrolyte.

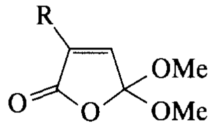
We tried to isolate $[Pd(tu)_3I]I$ by crystallization from methanol but obtained only a mixture of $[Pd(tu)_4]I_2$



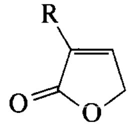
1a (R = Bu), 35%
1b (R = Ph), 29%
1c (R = $(CH_2)_3CN$), 33%



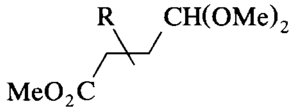
2a, 9%
2b, 4%
2c, 6%



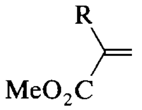
3a, traces
3b, 6%



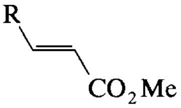
4a, 38%
4b, 39%
4c, 35%



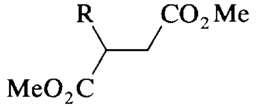
5a (R at C2), 3%
5′c (R at C3), 4%



6a, 7%
6b, 3%
6c, 3%



7a, 1%
7b, 3%
7c, 1%



8a, 1%
8b, 12%
8c, 2%

Table 1
Yields and conversions of alkyne carbonylation in the presence of complexes with different thiourea to palladium ratios under standard conditions

Catalyst	Substrate	Products									Time (h)	Total yield (%)	Total conversion (%)
		1	**2**	**3**	**4**	**5**	**5′**	**6**	**7**	**8**			
$[Pd(tu)_4]I_2$	**a**	1	0	0	1	0	0	0	0	0	24	2	2
	b	28	2	4	34	0	0	1	0	6	24	75	75
	c	26	4	0	27	0	3	3	0	1	24	64	64
$[Pd(tu)_2I_2]$	**a**	22	6	< 0.5	20	2	0	3	1	2	24	56	56
	b	22	4	0	26	0	0	6	4	26	24	88	88
	c	18	4	0	19	0	3	5	4	3	24	56	56
$[Pd(tu)_3I]I$	**a**	29	8	0	33	3	0	5	2	2	8	82	82
	b	26	4	6	35	0	0	6	7	14	5	98	98
	c	32	7	0	35	0	4	5	4	2	24	89	90
PdI_2 + 3.5tu	**a**	35	9	< 0.5	38	3	0	7	1	1	8	94	94
	b	29	4	6	39	0	0	3	3	12	6	96	96
	c	33	6	0	35	0	4	3	1	2	24	84	86

(which redissolves in methanol at the same concentration) and $[Pd(tu)_2I_2]$ (insoluble, see Experimental for separation). The species in solution therefore seems to be different from the sum of the last two. However, the literature [4b] reports equilibria involving this species. Its molecular weight by vapour pressure osmometry at 52°C (262–268) is nearer to that expected for $[Pd(tu)_3I]I$ (294) than to that for $[Pd(tu)_3]I_2$ (196). The conductivity ($\lambda = 89.4$ ohm^{-1} cm^2 mol^{-1} at 10^{-3} mol l^{-1}) falls in the range expected for 1 : 1 electrolytes (80–115).

The ^{13}C NMR spectra of the complexes containing 4 at 3 mol of thiourea are different in CD_3OD with resonance at 180.28 and 180.34 for the former and 180.74 for the latter. The spectrum of the complex with 2 mol of thiourea could not be determined owing to its low solubility. The presence of two resonances in the case of $[Pd(tu)_4]I_2$ is in accord with the existence of a partially dissociated species along with the fully dissociated species.

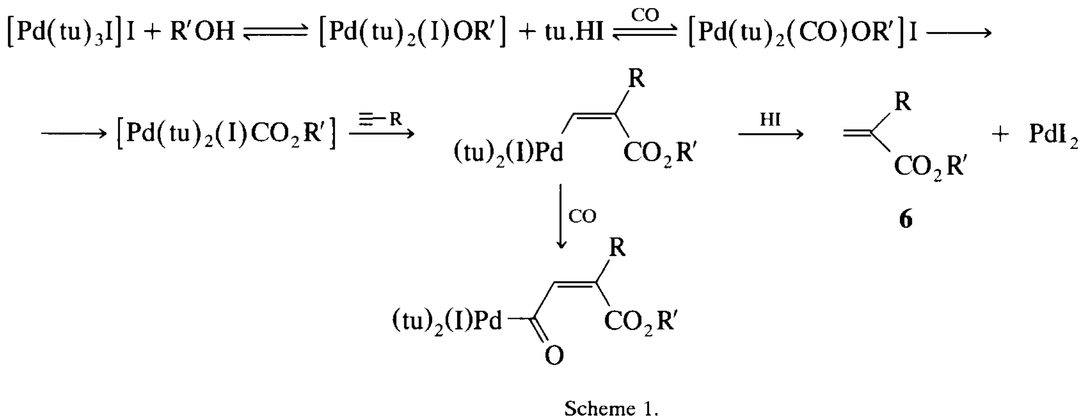
In conclusion, the experiments reported above support the assumption of the presence in solution of partially dissociated monomeric species in equilibrium with the iodide anion. This appears as a necessary condition for catalysis because a completely dissociated complex such as $[Pd(tu)_4](BF_4)_2$ is inactive.

A possible pathway is depicted in Scheme 1 for $Pd(tu)_3I_2$ as catalyst. Only the regioisomer leading to compound **6** is reported, but **7** is also present, as shown in Table 1. However, most of the products formed in subsequent steps derive from the precursor of **6**.

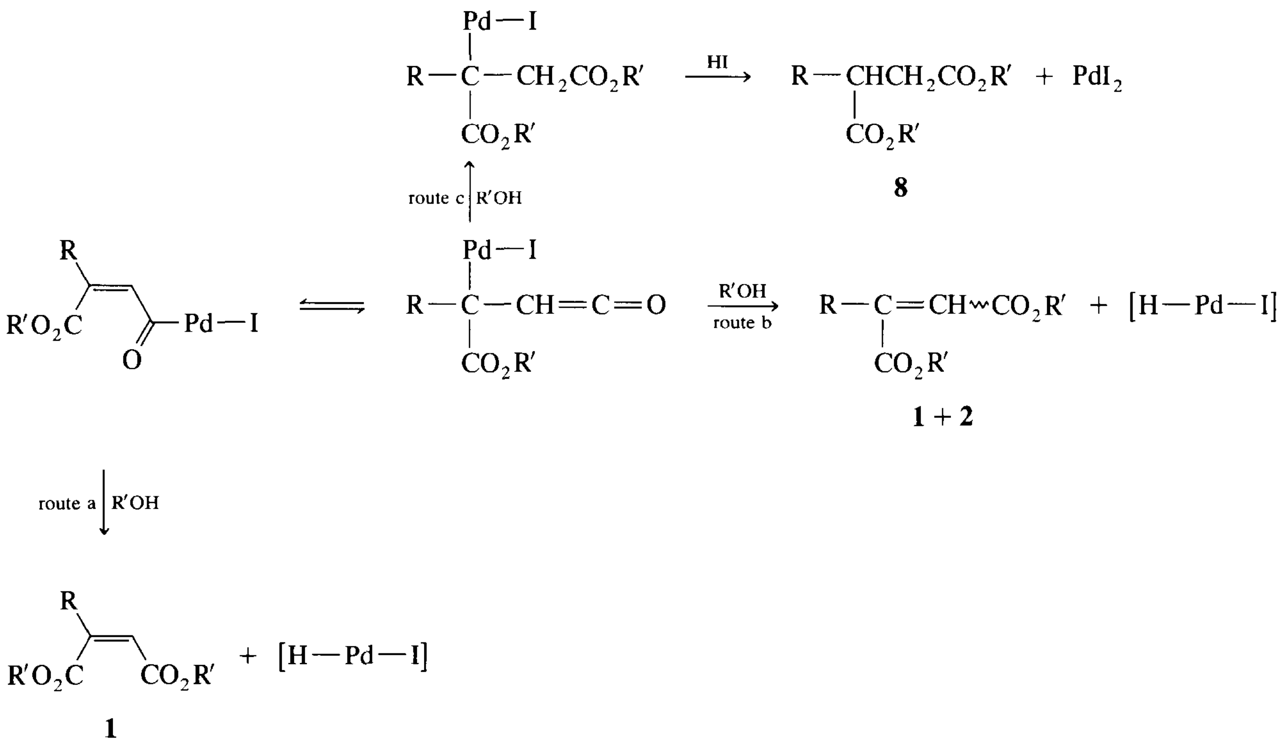
Dissociation and reassociation of the iodide and of thiourea allow coordination of the reactants and stabilization of the corresponding complexes. The first equilibrium (not reflected in MW and conductivity determinations) is strongly shifted to the left [5e]. Methoxycarbonylation is a well established step [5], followed by alkyne insertion [6,7]. Protonation leads to catalytic additive carbonylation to **6**, otherwise a new carbon monoxide insertion occurs.

On the basis of the isolation of compounds **1**–**8** and of the experiments and observations reported below, the way in which diesters are formed in conjunction with lactones and other reduction products can be tentatively rationalized. Thioureas are omitted for simplicity from the following schemes.

Diester formation can be thought to involve the acylpalladium species in different ways (routes a, b and c, as shown in Scheme 2), but only route a accounts for the selective formation of maleate **1**. A thiourea-stabilized H–Pd–I complex (or Pd^0 + HI; palladium metal



Scheme 1.



Scheme 2.

does not separate, but it could remain in solution [8]) would be formed concomitantly with the maleic ester.

The possible ketene tautomer shown in Scheme 2 may not account for the stereoselectivity of the reaction. It could be responsible for the formation of two minor products, the corresponding fumarate (route b) and succinate (route c). However, both of these products would be expected to form to a much larger extent if the ketene intermediate were involved in the main reaction leading to maleic ester **1**.

To understand the course of the reductive carbonylation step, the following points should be noted.

(1) The ratio between oxidative and reduction products is 1 : 1, so that other reducing agents, such as palladium hydride [9], obtained from methanol as observed by Portnoy and Milstein [9b], do not play a significant role.

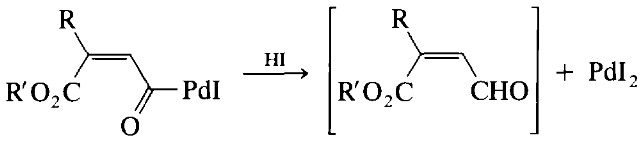
(2) The 1 : 1 ratio is observed even at low conversion. This means that as soon as H–Pd–I or Pd + HI are eliminated from the oxidative carbonylation step, another molecule must be reduced.

The reductive carbonylation products **4** and **5** could be viewed as originating from a 1,4- or 1,2-reduction of the unsaturated ester-aldehyde that could have been formed by protonation of the initial acylpalladium complex (Scheme 3) (protonation of acylmetal complexes to aldehydes has been reported [10]). However, the unsaturated ester-aldehyde was not present among the byproducts. Moreover, when the reaction was carried out in the presence of an unsaturated aldehyde such as cinnamaldehyde, no cinnamyl alcohol or its derivatives was observed and the saturated aldehyde (phenylpropionaldehyde) dimethyl acetal was formed only in trace amounts. Analogously, although the formation of succinic diester **8** could be ascribed to reduction of maleic diester **1**, no reduction to the corresponding saturated diester was obtained when a different maleic diester was added to the reaction mixture.

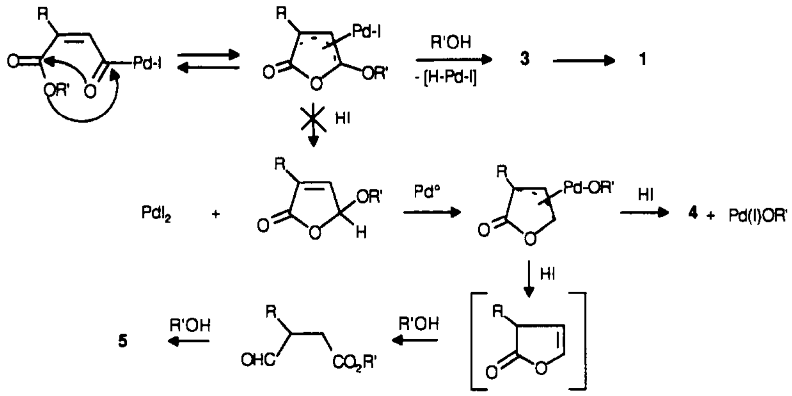
A pathway involving 5-alkoxyfuranones, as shown in Scheme 4, also has to be considered.

Nevertheless, 3-phenyl-5-methoxyfuranone was not detected among the byproducts of the reaction of phenylacetylene. Furthermore, when the reaction of hex-1-yne was carried out under our standard conditions in the presence of added 3-phenyl-5-methoxyfuranone [11], the latter was recovered unchanged.

The inference from these experiments is that the formation of lactone **4** must occur through hydride transfer to the palladium-bonded acyl group, otherwise



Scheme 3.



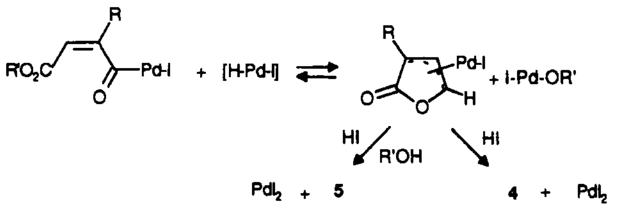
Scheme 4.

an alkoxyfuranone would be formed, which does not lead to the observed products. The possibility that ring formation is triggered by H–Pd–I, as shown in Scheme 5, would account for the products formed, but it is kinetically questionable.

We can postulate an alternative mechanism which involves a hydride transfer between two acyl chains within the same complex. Although stable complexes with two alkoxycarbonyl groups have been prepared [5], we believe that in our case the two acyl chains are likely to be formed by disproportionation, according to Scheme 6. This reaction, also named ''symmetrization'', readily occurs, in many cases reported in the literature [12], probably via dimerization. Hydrogen transfer would occur within the complex much like the hydrolysis of an acylmetal halide RCO–M–X, which gives RCOOR′ and HX, the difference in our case being that X is another acyl group.

In this context, it should also be recalled that the bis(lactonylidene) obtained by Tsuji and Nogi [13] in the carbonylation of alkynes in benzene possibly originated from the symmetrization reaction of a palladium-bonded lactonylidene precursor of our lactone. However, different from our case, the absence of protic solvents and the higher temperature (100°C) make the formation and dimerization of a palladium-bonded carbene reasonable.

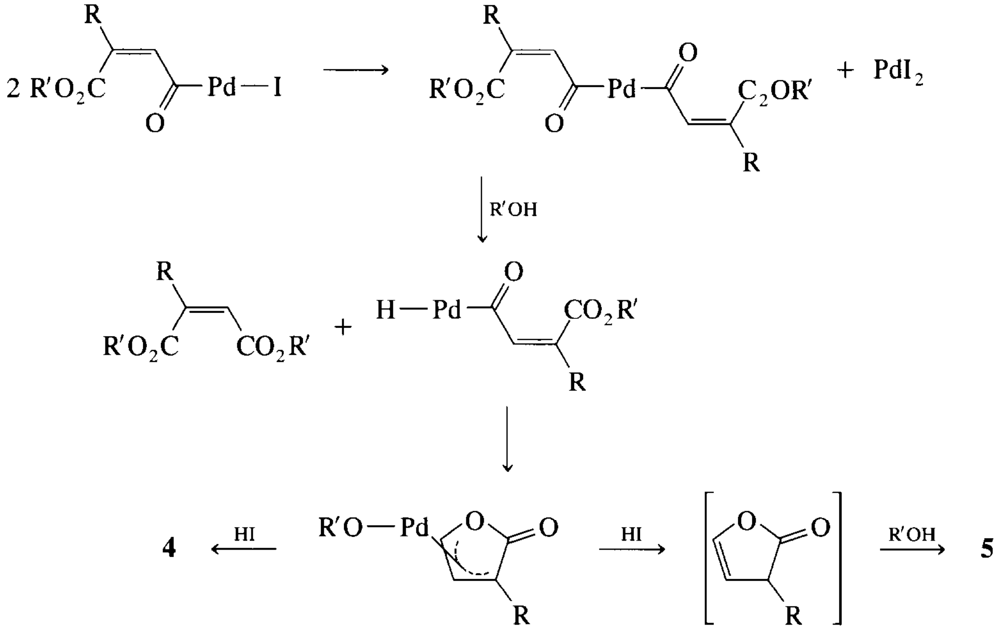
The process depicted in Scheme 6, which for the sake of simplicity does not include the tautomeric form of the acyl group shown in Scheme 4, thus appears to be consistent with the experimental observations listed above. Further work is needed to identify unequivocally the palladium complex involved.



Scheme 5.

So far we have considered the predominant regioisomer, which derives from initial attack of the alkoxycarbonyl group on the internal carbon of the triple bond. However, the monocarbonylation products include both types of regioisomer (**6** and **7**, from attack on the internal and terminal triply-bonded carbon). Further insertion of carbon monoxide appears to favour the species resulting from initial alkoxycarbonyl attack on the internal carbon. This can be understood if one considers that the terminal carbon–palladium bond thus formed is sterically more suitable for carbon monoxide insertion, while the internal palladium–carbon bond deriving from inverted regiochemistry inserts carbon monoxide less readily and is susceptible to competitive protonation to **7**. An anomalous behaviour is shown by the saturated semialdehyde acetal **5′c** (R′ = Me), which, unlike **5a**, shows inverted regiochemistry. This could be ascribed to chelation-promoted regioselectivity inversion, the chelating CN group contributing to the stabilization of the relevant carbon monoxide insertion intermediate. Formation of the lactone corresponding to **4c**, but with inverted regiochemistry, has not been observed. Apparently, the protonation site of the allylpalladium complex leading to the β,γ-unsaturated lactone and then to the saturated aldehyde is preferred to that leading to the α,β-unsaturated lactone, probably for steric reasons.

In conclusion, the products isolated from the catalytic carbonylation of alkynes with the PdI_2–thiourea system correspond to reductive and oxidative pathways, mediated by thiourea-stabilized Pd^{II} and Pd^0 compexes. The possible intervention of palladium(I) dimeric species [14] seems unlikely, although they may be present in intermediates which disproportionate to Pd^0 and Pd^{II}. Recent work by Drent et al. [15] on the monocarbonylation of alkynes shows that cationic palladium(II) species react in the same initial steps as we postulate for our



Scheme 6.

reaction. The special ligand (diphenyl-2-pyridylphosphine) then allows protonation of the monocarbonylated complex before the insertion of a new carbon monoxide molecule.

3. Experimental

Organic starting materials and compounds **7b** and **8b** were obtained from Aldrich and Merck. 5-Cyanopent-1-yne [16] and $[Pd(tu)_4]I_2$ [1c] were prepared according to literature procedures. Organic products **1a** [17], **2a** [17–19], **3a** [2], **4a** [20], **6a** [21], **7a** [22], **8a** [23], **1b** [19,24], **2b** [24], **3b** [2], **4b** [1a,25], **6b** [21], **1c** [7], **2c** [7], **6c** [26] and **7c** [22] were compared with those reported in the literature. New complexes and products are described below. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyser. The Pd : S and Pd : S : I ratios were determined by EDAX on a TRACOR X-ray 106-60 analyser. IR spectra were taken on a Perkin-Elmer System 2000 FTIR spectrometer and ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer (TMS as internal standard). Mass spectra were taken on an HP 5972A spectrometer. Molecular weight determinations were carried out on a Knauer vapour pressure osmometer. Conductivity measurements were obtained with an LKB 5300B conductolyser conductivity bridge. The reaction mixtures were analysed by TLC (SiO_2) or GLC on capillary type HP-5 columns (30 m × 0.25 mm i.d.; polymethylsilicone + 5% phenylsilicone as stationary phase). Quantitative determinations were carried out by GLC with an internal standard. Separation of the products was by column chromatography (Merck silica gel 60, 70–230 mesh) after filtration from palladium metal.

3.1. Preparation of complexes

$[Pd(tu)_4]$ $[BF_4]_2$

To 200 mg (0.45 mmol) of $[Pd(MeCN)_4][BF_4]_2$ [27] dissolved in 2 ml of dry MeCN under dinitrogen, 137 mg (1.80 mmol) of thiourea were added at 20°C. The solution changed from yellow to orange. Diethyl ether was slowly added in an excess and a crystalline orange–red solid precipitated on standing. After drying it weighed 250 mg (95% yield). The complex is stable in air.

Elemental Anal.: Found: C, 8.25; H, 2.77; N, 19.30; $C_4H_{16}B_2F_8N_8PdS_4$ Calc: C, 8.22; H, 2.76; N, 19.17%. Pd : S = 1 : 3.97. IR (KBr) (cm^{-1}): 3409(m), 3347(s), 3276(s), 3179(s), 1627(s), 1612(s), 1505(w), 1432(m), 1389(m), 1000–1100 (broad), 711(w), 638(w), 522(m), 471(w).

Osmometric and conductivity (10^{-3} mol l^{-1}) measurements are reported in the text for this and the following complexes.

$[Pd(tu)_4]I_2$ [14]

We add here more accurate IR determinations (KBr) (cm^{-1}): 3416(m), 3340(s), 3269(s), 3181(s), 3147(s), 1622(s), 1607(s), 1499(w), 1427(m), 1381(s), 1083(vw), 709(m), 615(m), 467(w).

$[Pd(tu)_2I_2]$

Into a 100 ml flask were introduced 400 mg (1.11 mmol) of PdI_2, 169 mg (2.22 mmol) of thiourea and 28 ml of methanol and the mixture was stirred for 8 h at 20°C. A brick-red powder (490 mg, 86%) was filtered off and dried under vacuum.

Elemental Analy.: Found: C, 4.59; H, 1.53; N, 10.87; $C_2H_8I_2N_4PdS_2$ Calc.: C, 4.69; H, 1.56; N, 10.93%. Pd : S : I = 1 : 2.12 : 2.04. IR (KBr) (cm^{-1}): 3420(m), 3387(s), 3300(s), 3275(s), 3182(m), 1614(s), 1604(s), 1431(m), 1393(s), 711(w), 486(m), 468(m).

PdI_2 + 3tu

Into a 100 ml flask were introduced 100 mg (0.28 mmol) of PdI_2, 63.4 mg (0.83 mmol) of thiourea and 56 ml of methanol and the mixture was stirred for 0.5–1 h at 20°C until a homogeneous orange–red solution was obtained. Evaporation of the solvent gave a mixture of brick-red powder $[Pd(tu)_2I_2]$ and orange–red crystals $[Pd(tu)_4]I_2$. The former, which did not dissolve in methanol (polymeric form), was separated by filtration and compared with a sample prepared according to the procedure described above. The solution contained $[Pd(tu)_4]I_2$, which was compared with an authentic sample.

3.2. Carbonylation procedure

Into a 25 ml flask with side-arm were introduced 50 mg (0.139 mmol) of PdI_2 and 32 mg (0.420 mmol) or 37 mg (0.486 mmol) of thiourea. Air was displaced by carbon monoxide and a solution of the substrate, 2.78 mmol, in 7 ml of methanol was added under CO at 20°C. The solution was magnetically stirred for the required time.

Products **6a**, **2a**, **1a**, **5a** (in a mixture with **1a**) and **4a** were eluted in this order using a concentration gradient of hexane–ethyl acetate from 98 : 2 to 50 : 50. Products **7a**, **8a** and **3a** were compared with pure products by GLC–MS; **8a** was obtained by catalytic hydrogenation of **1a**.

Products **6b**, **7b**, **3b**, **2b**, **8b**, **1b** and **4b** were eluted in this order using a concentration gradient of hexane–ethyl acetate from 95 : 5 to 50 : 50 in a silica gel chromatographic column. Products **6c**, **2c**, **5′c** (in a mixture with **1c**, 1 : 1 ratio), **1c** and **4c** were eluted in this order using a concentration gradient of hexane–ethyl acetate from 80 : 20 to 50 : 50. Product **5′c** was identified by ^1H NMR spectroscopy directly in the mixture with **1c**. Products **7c** and **8c** (obtained in small amounts) could not be isolated. They were identified by GLC–MS comparison with pure products obtained from catalytic hydrogenation of **1c** in the case of **8c** and from literature data [21] in the case of **7c**.

Compound **5a** was obtained in 1 : 1 mixture with **1a**. Signals reported here refer to **5a** only. GLC–MS (*m/z*): M^+ (218) absent, 217 (< 1), 203 (< 1), 187 (10), 171 (< 1), 143 (< 1), 130 (1), 127 (11), 115 (1), 101 (1), 95 (3), 89 (4), 87 (2), 85 (1), 76 (3), 75 (100), 71 (12), 69 (2), 67 (1), 59 (3), 58 (4), 55 (4), 53 (1). ^1H NMR (300 MHz, $CDCl_3$), δ: 0.88 (t, 3H, J = 7.0 Hz, *Me*); 1.20–1.50 (hidden signal, 1H, CHHCHCO$_2$Me); 1.20–1.30 (m, 4H, CH_2CH_2Me); 1.55–1.64 (m, 1H, CH-HCHCO$_2$Me); 1.70 (ddd, 1H, J = 14.0, 6.0 and 4.4 Hz, CHHCH(OMe)$_2$; 2.00 (ddd, 1H, J = 14.0, 9.9 and 5.4 Hz, CHHCH (OMe)$_2$; 2.49 (m, 1H, CHCO$_2$Me); 3.31 (s, 6H, (OMe)$_2$); 3.69 (s, 3H, CO$_2$$Me$); 4.36 (dd, 1H, J = 6.0 and 5.5 Hz, CH(OMe)$_2$). All the attributions were confirmed by a 2D-COSY experiment.

Compound **4c** was obtained as a colourless oil. MS (*m/z*): 151 (M^+, 1), 150 (3), 134 (9), 124 (3), 123 (19), 122 (56), 111 (16), 107 (10), 106 (7), 99 (5), 98 (100), 97 (22), 95 (11), 94 (33), 93 (25), 83 (16), 79 (12), 77 (9), 69 (17), 68 (11), 67 (97), 66 (10), 65 (17), 55 (13), 54 (22), 53 (32). IR (film) (cm^{-1}): 2941(m), 2874(w), 2246(m), 1748(s), 1653(w), 1451(m), 1351(m), 1205(m), 1168(w), 1085(s), 1060(s), 946(w), 834(m). ^1H NMR (300 Mhz, $CDCl_3$), δ: 1.97 (pseudo-quintuplet, 2H, J = 7.6 Hz, CH_2CH$_2$CN); 2.43 (t, 2H, J = 7.0 Hz, CH$_2$CN); 2.50 (pseudo-tq, 2H, J = 7.9, 1.7 and 1.7 Hz, CH$_2$C=C); 4.83 (pseudo-q, 2H, J = 1.7 Hz, CH$_2$O); 7.28 (pseudo-quintuplet, 1H, J = 1.7 Hz, CH=).

Compound **5′c** was obtained in a 1 : 1 mixture with **1c**. Signals reported here refer to **5′c** only. GLC–MS (*m/z*):229 (M^+, < 1), 228 (< 1), 214 (< 1), 198 (2), 182 (< 1), 166 (2), 138 (25), 124 (1), 106 (1), 101 (2), 97 (2), 85 (3), 81 (1), 79 (2), 76 (3), 75 (100), 71 (5), 69 (1), 67 (2), 59 (3), 55 (5), 53 (2). ^1H NMR (300 MHz, $CDCl_3$), δ: 1.37–1.46 (m, 1H, CHHCH); 1.60–1.67 (m, 1H, CHHCH); 1.70 (pseudo-quintuplet, 2H, J = 6.8, CH_2CH$_2$CN); 2.20–2.27 (m, 1H (CHCH(OMe)$_2$); 2.24 (distorted dd, 1H, J = 17.9 and 6.8 Hz, CHHCO$_2$Me); 2.36 (t, 2H, J = 7.0 Hz, CH$_2$CN); 2.49 (distorted dd, 1H, J = 18.0 and 8.2 Hz, CHHCO$_2$Me); 3.38 (s, 6H, 2 OMe); 3.69 (s, 3H, CO$_2$Me); 4.19 (d, 1H, J = 5.0, CH(OMe)$_2$). All the assignments were confirmed by a 2D-COSY experiment.

Compound **8c** was obtained as a colourless oil. MS (*m/z*): 213 (M^+, absent), 182 (30), 181 (7), 173 (4), 154 (38), 149 (8), 146 (21), 141 (27), 140 (42), 138 (6), 127 (11), 123 (6), 122 (64), 121 (19), 115 (11), 114 (58), 113 (20), 112 (9), 110 (6), 109 (4), 108 (51), 101 (9), 99 (5), 95 (10), 94 (100), 93 (13), 87 (6), 85 (6), 81 (14), 74 (22), 71 (28), 69 (12), 68 (28), 67 (43), 66 (6), 65 (6), 59 (65), 55 (74), 54 (12), 53 (19). IR (film) (cm^{-1}): 2959(s), 2246(w), 1737(s), 1438(m), 1262(s), 1160(s), 1110(s), 1079(s), 1057(s), 1013(s), 796(m), 761(m). ^1H NMR (300 MHz, $CDCl_3$), δ: 1.64–1.80 (m, 4H, CH_2CH_2CH$_2$CN); 2.36 (t, 2H, J = 6.8 Hz, CH$_2$CN); 2.44 (distorted dd, 1H, J = 16.4 and 5.5 Hz, CHHCO$_2$Me); 2.74 (distorted dd, 1H, J = 16.4 and 8.6 Hz, CHHCO$_2$Me), 2.87 (m, 1H, CHCO$_2$Me); 3.67 (s, 3H, CO$_2$Me); 3.70 (s, 3H, CO$_2$Me).

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References

[1] (a) G.P. Chiusoli, M. Costa, P. Pergreffi, S. Reverberi and G. Salerno, *Gazz. Chim. Ital.*, *115* (1985) 691; (b) A. Bonardi, B. Gabriele, M. Costa, G. Salerno and G.P. Chiusoli, *J. Chem. Soc., Chem. Commun.*, (1994) 2429; (c) M. Costa, L. De Sousa Santos, G.P. Chiusoli, B. Gabriele and G. Salerno, *J. Mol. Catal.*, *78* (1993) 151.

[2] B. Gabriele, M. Costa, G. Salerno and G.P. Chiusoli, *J. Chem. Soc., Perkin Trans. 1*, (1994) 83.

[3] G. De Munno, B. Gabriele, G. Salerno *Inorg. Chim. Acta*, *234* (1995) 181.

[4] (a) W.J. Geary, *Coord. Chem. Rev.*, *7* (1971) 81; (b) V.I. Shlenskaya, A.A. Biryukov and E.M. Moskovskina, *Zh. Neorg. Khim.*, *11* (1966) 600

[5] (a) U. Romano and F. Rivetti, *J. Organomet. Chem.*, *154* (1978) 323; (b) D. Milstein, *Acc. Chem. Res.*, *21* (1988) 428 and references cited therein; (c) Y. Kim, K. Osakada, K. Sujita, T. Yamamoto and A. Yamamoto, *Organometallics*, *7* (1988) 2182; (d) H.E. Bryndza and W. Tam, *Chem. Rev.*, *88* (1988) 1163; (e) G.D. Smith, B.E. Hanson, J.S. Merola and F.J. Waller, *Organometallics*, *12* (1993) 568; (f) R. Bertani, G. Cavinato, L. Toniolo and G. Vasapollo, *J. Mol. Catal.*, *84* (1993) 165.

[6] (a) T.F. Murray and J.R. Norton, *J. Am. Chem. Soc.*, *101* (1979) 4107; (b) 106 (1984) 5505; (c) O.N. Temkin and L.G. Bruk, *Abstr. Soviet–Japanese Seminar on Catalysis, Novosibirsk, 1990*, 1990, p. 83.

[7] D. Zargarian and H. Alper, *Organometallics*, *10* (1991) 2914, and references cited therein.

[8] (a) T. Mandai, T. Matsumoto and J. Tsuji, *Tetrahedron Lett.*, *34* (1993) 2513; (b) C. Amatore, A. Jutand and M.A.M. Barki, *Organometallics*, *11* (1992) 3009; (c) F. Ozawa, A. Kubo and T. Tayashi, *Chem. Lett.*, (1992) 2177.

[9] (a) M. Portnoy, F. Frolow and D. Milstein, *Organometallics*, *10* (1991) 3960; (b) M. Portnoy and D. Milstein, *Organometallics*, *13* (1994) 600; (c) D.L. Reger and D.G. Garza, *Organometallics*, *12* (1993) 554; (d) B.T. Heaton, S.P. A. Hébert, J.A. Iggo, F. Metz and R. Whyman, *J. Chem. Soc., Dalton Trans.*, (1993) 3081; (e) T. Chenal, R. Naigre, I. Ciprès, P. Kalck, J. Daran and J. Vaissermann, *J. Chem. Soc., Chem. Commun.*, (1993) 747; (f) M. Sommovigo, M. Pasquali, P. Leoni, P. Sabatino and D. Braga, *J. Organomet. Chem.*, *418* (1991) 119, and references cited therein.

[10] J.A. Marsella, J.C. Huffmann, K.G. Caulton, B. Longato and J.R. Norton, *J. Am. Chem. Soc.*, *104* (1982) 6360; B.K. Campion, J. Falk and T. Don Tilly, *J. Am. Chem. Soc.*, *109* (1987) 2049.

[11] I.L. Doer and R.E. Willett, *J. Org. Chem.*, *38* (1973) 3878.

[12] I.V. Kozhevnicov and K.I. Matveev, *Russ. Chem. Rev.*, *47* (1978) 649.

[13] J. Tsuji and T. Nogi, *J. Am. Chem. Soc.*, *88* (1966) 1289.

[14] L.G. Bruck, O.N. Temkin, Z.V. Goncharova, I.S. Ustenko and V.R. Flid, *React. Kinet. Catal. Lett.*, *9* (1978) 308.

[15] E. Drent, P. Arnoldy and P.H.M. Budzelaar, *J. Organomet. Chem.*, *455* (1993) 247.

[16] G. Eglinton and M.C. Whiting, *J. Chem. Soc.*, (1953) 3052.

[17] R. Fittig and F. Fichter, *Liebigs Ann. Chem.*, *304* (1899) 241.

[18] E.R.H. Jones, T.Y. Shen and M.C. Whiting, *J. Chem. Soc.*, (1951) 48.

[19] R.F. Heck, *J. Am. Chem. Soc.*, *94* (1972) 2712.

[20] M. Watanabe, S. Nakamori, H. Hasegawa, K. Shirai and T. Kumamoto, *Bull. Chem. Soc. Jpn.*, *54* (1981) 817.

[21] E.R.H. Jones, T.Y. Shen and M.C. Whiting, *J. Chem. Soc.*, (1950) 230.

[22] R.C. Larock, *J. Org. Chem.*, *40* (1975) 3237.

[23] H. Stetter and H. Meisel, *Chem. Ber.*, *90* (1957) 2928.

[24] E.C. Taylor, Jr., and E.J. Strojny, *J. Am. Chem. Soc.*, *76* (1954) 1872.

[25] G. Swain, A.R. Todd and W.S. Waring, *J. Chem. Soc.*, (1944) 548.

[26] E.R.H. Jones, G.H. Whithan and M.C. Whiting, *J. Chem. Soc.*, (1954) 1865.

[27] T.W. Lai and A. Sen, *Organometallics*, *3* (1984) 866.