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Further studies of the Pt(II) catalyzed hydromethoxycarbonylation of 1-alkynes

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Abstract

Pt(II) complexes such as $PtCl_2(PPh_3)_2$, $PtHCl(PPh_3)_2$, $PtHCl(PEt_3)_2$, $PtH(NO_3)(PEt_3)_2$, $PtCl_2$(1,4-bis(diphenylphosphino)butane) are able to catalyze the hydromethoxycarbonylation of phenylacetylene. It has been found that the dichloro complexes require the presence of $SnCl_2$ to be active in catalysis, while the hydrido species do not require the presence of promotors. Among the catalysts tested $PtHCl(PPh_3)_2$ displays the highest activity accompanied by a total regioselectivity towards the formation of methyl atropate, however the chemoselectivity of the reaction is only ≈40–60% owing to formation of high molecular weigh by-products due to partial polymerization both of the substrate and of the carbonylation product. It is interesting to note that working with $PtCl_2$(1,4-bis(diphenylphosphino)butane) the regiochemistry of the reaction is inverted and the main product is methyl cinnamate. Some aspects of the mechanism are discussed.

Keywords: 1-Alkyne; Carbonylation; Platinum

1. Introduction

The hydroalkoxycarbonylation of 1-alkynes is a very important tool for the synthetic and industrial organic chemistry, however it is necessary to develop new more active catalytic systems able to afford complete control of the regioselectivity of the reaction. For instance the hydromethoxycarbonylation of 1-phenylacetylene can afford α-methylene-benzeneacetate (methyl atropate) **1** and 3-phenyl-2-propenoate (methyl cinnamate) **2** (see Scheme 1)

Methyl cinnamate is a versatile intermediate which can be converted into valuable organic products such as phenylalanine or phenylsuccinic acid [1]. Methyl atropate is representative of α-aryl propenoic acids or esters which can be hydrogenated to the corresponding α-aryl propionic acids or esters [2,3]. These compounds belong to the NSAI (non-steroidal antiinflammatory) class of drugs which commercial importance is rapidly increasing [4].

The catalytic or stoichiometric hydroalkoxycarbonylation of acetylenic substrates is usually carried out in the presence of transition metal complexes of the first and second row of group 8 [5–8]. As far as the use of platinum catalysts is concerned, there is only one study which reports that complexes of Pt(II) in the presence of $SnCl_2$ display moderate activity accompanied by an excellent regioselectivity towards the formation of the more branched product [9]. This latter feature

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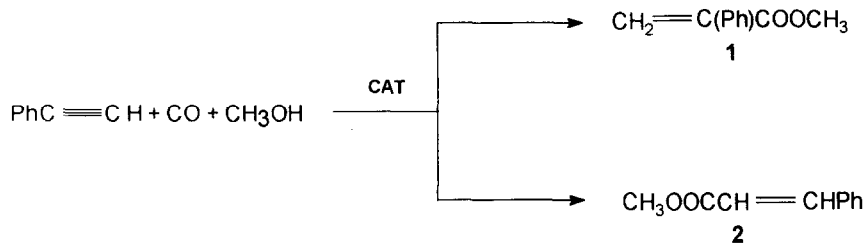


Scheme 1.

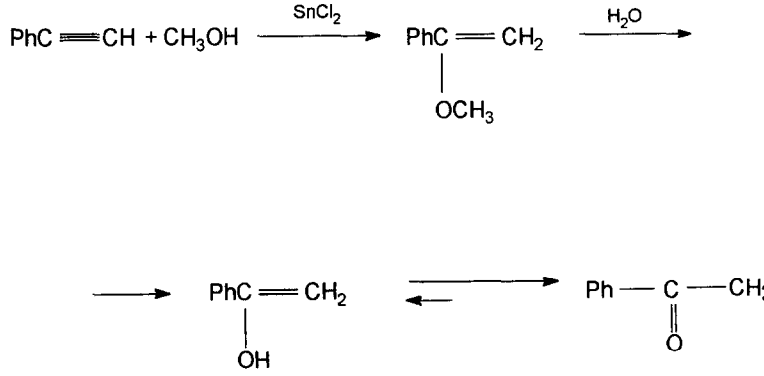
prompted us to undertake a systematic study on the carbonylation of phenylacetylene in the presence of Pt(II) species. A preliminary account of our work which reports the excellent regioselectivity control attainable with these catalysts has been already published [10]. Here, we describe more thoroughly our investigations.

2. Results

Owing to our interest in the synthesis of atropic acid homologues, phenylacetylene was employed as the model substrate. At first, the carbonylation experiments were carried out under the conditions reported by Tsuji et al. [9] i.e., using $PtCl_2(PPh_3)_2$ as catalyst precursor (substrate to platinum molar ratio = 200) in the presence of $SnCl_2$ as promoter (Sn/Pt = 5) at 80°C under 80 bar of initial carbon monoxide pressure (reaction time = 18 h) in methanol. GLC–MS analysis indicates that under the above conditions the main product is acetophenone and that the desired methyl atropate is formed only in very low yield (< 1%). This result can be rationalised by invoking a tin catalysed addition of methanol to the carbon–carbon triple bond, followed by hydrolysis and tautomerization as depicted in Scheme 2.

The proof of such a mechanism is beyond the scope of the present study, but if it is operative the formation of acetophenone could be reduced working with a lower Sn/Pt molar ratio and using stoichiometric amounts of methanol. In fact, when we use a Sn/Pt ratio = 1 and a methanol to substrate molar ratio = 2 in the presence of an organic solvent, the main product of the reaction is methyl atropate **1**. The dependence of the yield of the products of the reaction on the solvent and the relevant reaction conditions are reported in Table 1.

As can be seen from the data of Table 1 the sum of the yields in methyl atropate and acetophenone is not consistent with the conversion of the substrate. This is due to the formation of by-products not detectable in GLC. As a matter of fact, IR and



Scheme 2.

Table 1
The hydromethoxycarbonylation of phenylacetylene in the presence of the catalytic system $PtCl_2(PPh_3)_2/SnCl_2 \cdot 2H_2O$ [a,b]

Solvent	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Acetophenone yield (%)
Tetrahydrofuran	41.6	9.4	–	31.3	0.9
Toluene	30.0	9.9	tr	18.3	1.8
Dichloromethane	31.5	4.8	–	25.2	1.5
Acetone	38.2	7.6	tr	29.8	0.8
Acetonitrile	22.3	1.2	–	21.1	–

[a] Reaction conditions: $T = 100°C$, $P(CO) = 100$ atm, reaction time = 22 h, phenylacetylene = 10 mmol, methanol = 20 mmol, solvent = 10 ml, Pt/substrate = 1/200, Pt/Sn = 1/1.
[b] tr = traces.

NMR analyses carried out on the residues obtained by taking to dryness the reaction crudes indicate both the formation of poly(phenylacetylene) [11,12] and of other polymeric products deriving from methyl atropate. In this connection it is noteworthy that platinum (II) complexes are able to promote the polymerisation of phenylacetylene [13,14] and that owing to its unique structure methyl atropate is expected to undergo thermal polymerisation [15].

Apart from acetonitrile, the nature of the solvent exerts a very little influence on the reaction course. The most intriguing results are related to the regioselectivity of the reaction since methyl atropate is almost the only non-polymeric species which forms regardless the reaction solvent.

Both the substrate conversion and the yield in methyl atropate are much improved using $PtHCl(PPh_3)_2$ instead of $PtCl_2(PPh_3)_2$. Table 2 reports the data obtained in various solvents. Also with this catalyst, the nature of the solvent does not affect neither the chemo- nor the regioselectivity of the reaction. It is to point out that the formation of acetophenone is very low and that methyl atropate is the only regioisomer produced.

Looking for higher activity and chemoselectivity we tested also the system $PtCl_2$(DPPB)/$SnCl_2$ (DPPB = 1,4-bis(diphenylphosphino)butane) which is known to be very active in the hydroformylation of olefins [16]. The conditions used and the dependence of the catalytic activity on the solvent are reported in Table 3.

This catalyst produces predominantly the linear regioisomer methyl cinnamate **2**. At variance of that observed using the monophosphine derivatives, the solvent plays a substantial role in determining the regioselectivity since the cinnamate/atropate ratio is about 3 in tetrahydrofuran, becomes close to 7 in acetone and is higher than 30 in a less polar solvent like toluene. This result is outstanding and as we have already accounted for the same inversion of regiochemistry was observed when we used a completely aliphatic substrate such as 1-heptyne, thus demonstrating

Table 2
The hydromethoxycarbonylation of phenylacetylene in the presence of the catalytic system $PtHCl(PPh_3)_2/SnCl_2 \cdot 2H_2O$ [a,b]

Solvent	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Acetophenone yield (%)
Tetrahydrofuran	50.4	20.2	–	30.2	–
Toluene	34.5	14.1	–	20.4	tr
Dichloromethane	47.7	20.0	–	27.7	tr
Acetone	44.4	16.9	–	27.5	–

[a] Reaction conditions: $T = 100°C$, $P(CO) = 100$ atm, reaction time = 22 h, phenylacetylene = 10 mmol, methanol = 20 mmol, solvent = 10 ml, Pt/substrate = 1/200, Pt/Sn = 1/1.
[b] tr = traces.

Table 3
The hydromethoxycarbonylation of phenylacetylene in the presence of the catalytic system $PtCl_2(DPPB)/SnCl_2 \cdot 2H_2O$ [a,b]

Solvent	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Acetophenone yield (%)
Tetrahydrofuran	99.5	10.8	28.9	59.8	tr
Toluene	97.1	1.0	34.3	61.8	tr
Dichloromethane	93.0	–	7.6	85.4	tr
Acetone	59.5	1.0	6.6	51.9	tr

[a] Reaction conditions: $T = 100°C$, $P(CO) = 100$ atm, reaction time = 22 h, phenylacetylene = 10 mmol, methanol = 20 mmol, solvent = 10 ml, Pt/substrate = 1/200, Pt/Sn = 1/1.
[b] tr = traces.

Table 4
The hydromethoxycarbonylation of phenylacetylene in the presence of the catalytic system $PtHCl(PPh_3)_2$ and variable amounts of $SnCl_2 \cdot 2H_2O$ [a]

$SnCl_2 \cdot 2H_2O$ (mmol)	Sn/Pt	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Acetophenone yield (%)
0	0/1	65.0	26.8	–	38.2	–
0.05	1/1	50.4	20.3	–	30.1	–
0.1	2/1	32.5	9.8	–	21.2	1.5

[a] Reaction conditions: $T = 100°C$, $P(CO) = 100$ atm, reaction time = 22 h, phenylacetylene = 10 mmol, methanol = 20 mmol, tetrahydrofuran = 10 ml, Pt/substrate = 1/200.

Table 5
The hydromethoxycarbonylation of phenylacetylene in the presence of the complex $PtHCl(PPh_3)_2$ [a]

Solvent	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Acetophenone yield (%)
n-Heptane	98.2	35.8	–	62.4	–
Toluene	92.2	45.2	–	47.0	–
Methanol	98.5	13.4	–	78.3	6.8
Tetrahydrofuran	65.0	26.8	–	38.2	–
Dichloromethane	61.1	25.3	–	35.8	–
Acetone	56.5	21.8	–	34.7	–

[a] Reaction conditions: $T = 100°C$, $P(CO) = 100$ atm, reaction time = 22 h, phenylacetylene = 10 mmol, methanol = 20 mmol, solvent = 10 ml, Pt/substrate = 1/200.

that this regioselectivity control is independent of the peculiar nature of the substrate [10]. Apart from acetone, this catalytic system gives very high substrate conversions independently of the nature of the solvent. However, the yield in carbonylation products is rather poor owing to the formation of large amounts of polymeric by-products.

Since the goal of our researches is the synthesis of atropic acid and its derivatives, we decided to investigate more extensively the use of monophosphine substituted platinum(II) species. Therefore we tested the catalytic activity of the hydrido complex $PtHCl(PEt_3)_2$ in the presence of one equivalent of $SnCl_2$. Under the conditions used with the other catalysts, this species produced mostly polymeric materials and only small quantities of methyl atropate and acetophenone.

From the data of Tables 1–3 it appears that the system $PtHCl(PPh_3)_2/SnCl_2$ in tetrahydrofuran displays the highest catalytic activity, therefore we tried to optimize this system varying the Sn to Pt ratio (Table 4). Unexpectedly the data of Table 4 demonstrate that the hydrido-chloro-platinum complex does not need the presence of $SnCl_2$ to

Table 6
The hydromethoxycarbonylation of phenylacetylene in the presence of the complex $PtHCl(PPh_3)_2$ under different $P(CO)$ [a]

$P(CO)$ [b] (atm)	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Methyl atropate/polymer ratio
50	39.5	16.4	–	23.1	0.7
100	65.6	30.4	–	35.2	0.9
160	85.9	45.7	–	40.2	1.1
250	98.1	55.6	–	42.5	1.3

[a] Reaction conditions: $T = 100°C$, reaction time = 15 h, phenylacetylene = 10 mmol, methanol = 20 mmol, toluene = 10 ml, Pt/substrate = 1/200.
[b] Measured at room temperature.

Table 7
The hydromethoxycarbonylation of phenylacetylene in the presence of the complex $PtHCl(PPh_3)_2$ at different temperatures [a]

T (°C)	Conversion (%)	Methyl atropate yield (%)	Methyl cinnamate yield (%)	Polymers yield (%)	Methyl atropate/polymer ratio
50	13.6	9.8	–	3.8	2.6
80	37.1	23.3	–	13.8	1.7
90	60.8	35.8	–	25.0	1.4
100	98.1	55.6	–	42.5	1.3

[a] Reaction conditions: $P(CO) = 250$ bar at r.t., reaction time = 15 h, phenylacetylene = 10 mmol, methanol = 20 mmol, toluene = 10 ml, Pt/substrate = 1/200.

be able to catalyze the reaction. In fact, its presence damages both the activity and the chemoselectivity of the reaction. This finding prompted us to revise the effect of the solvent, temperature and $P(CO)$ on the reaction. Table 5 reports the catalytic activity of complex $PtHCl(PPh_3)_2$ in some different solvents.

In contrast to that observed with the systems Pt(II)/Sn(II) the solvent influences the reaction which proceeds at best in media of low polarity such as n-heptane and toluene; this latter gives the best results since it allows good conversion accompanied by the highest yield in methyl atropate. The catalyst is completely regioselective regardless of the solvent used, moreover the formation of acetophenone is observed only in neat methanol.

The dependence of the catalytic activity on the $P(CO)$ is reported in Table 6. An increase of the $P(CO)$ leads to an enhancement of the substrate conversion and of the chemoselectivity of the reaction since the methyl atropate/polymer ratio roughly doubles on increasing the $P(CO)$ from 50 to 250 bar.

In order to obtain further enhancement of the chemoselectivity we have carried out the reaction at temperatures lower than 100°C. The relevant data are presented in Table 7. As expected on lowering the reaction temperature the chemoselectivity increases because the polymer formation is reduced. However, in order to get a substantial increase of the chemoselectivity, it is necessary to carry out the reaction at temperatures so low ($\leq 50°C$) that it follows an important loss in catalytic activity and hence an useless reaction rate.

3. Discussion

In our opinion the most important results of the present investigations are the finding that $PtHCl(PPh_3)_2$ does not need the presence of a tin halide to be active in catalysis and the observation that a convenient selection of the catalytic species allows to obtain a complete control of the regioselectivity of the reaction.

The first finding, which has obvious implications on practical aspects of the catalytic process

such as the recovery and the recycle of the catalyst, does not contrast with the data reported by Tsuji and co-workers [9] since these authors did never test the catalytic activity of platinum hydrides in the absence of tin chloride. We are brought to believe that the key ligand is the hydride. As a matter of fact, some experiments we have not reported for sake of brevity demonstrate that also complex $PtH(NO_3)(PEt_3)_2$ is able to catalyze the reaction even if its activity is lower than that of $PtHCl(PPh_3)_2$. Therefore the first step of the reaction probably implies the insertion of the alkyne into a Pt–H bond to give a σ-vinyl intermediate. It is noteworthy that this reaction which has been subject of detailed studies [17–20] proceeds smoothly under very mild conditions.

The fine details of this step are of the utmost importance since it also settles the regiochemistry of the catalytic process therefore it is worthy of some additional comment. During his investigations, Clark [19,20] observed that the regiochemistry of the insertion of an alkyne into a Pt–H bond is affected by several factors including the solvent and the basicity of the phosphine ligands. In particular, among Clark's observations two are of particular relevance for the present work, i.e., (i) in model reactions, the presence of CO coordinated to the platinum can reverse the usual regiochemistry obtained in its absence and (ii) a critical role is also played by the ligand *trans* to the hydride. Our experiments indicate that using $PtHCl(PPh_3)_2$ the regioselectivity of the catalytic process is insensitive to factors such as the solvent and the basicity of the ligands therefore we are led to attribute this behavior to a compelling influence exerted by CO. Also in the case of the system $PtCl_2$(DPPB)/$SnCl_2$ the actual catalytic species is probably a diphosphine–platinum–hydride complex having a phosphorus ligand in *trans* position to the hydride. Thus the reverse of regiochemistry observed with this catalyst could be attributable to the high difference existing between the *trans* influence of a phosphorus ligand with respect to that of an halide ion.

Two major pathways are thought to be operative immediately after the formation of a metal–alkyl moiety [21]. The first one involves the CO insertion into the M–C bond to form an acylmetal complex, which upon alcoholysis affords the carboxylic esters. Alternatively, the reaction could involve the reductive coupling of the alkyl moiety with an alkoxycarbonyl group formed by the formal CO insertion into an M–OR bond. In the case of the Pt(II) chemistry the relevant model processes have been studied by Stang and co-workers [22,23]. Their results demonstrate that the first pathway is more likely in the case of vinyl platinum (II) complexes having halides as counter ions, while the second one is probably operative when the platinum metal center has weakly coordinating counterions such as triflates.

4. Experimental

GLC analyses were carried out on a Hewlett-Packard HP 5890 gas chromatograph. GLC–MS spectra were obtained with a Hewlett-Packard HP 5890 gas chromatograph interfaced to a HP 5871 quadrupole mass detector. The platinum(II) complexes $PtCl_2(PPh_3)_2$ [24], $PtHCl(PPh_3)_2$ [24], $PtHCl(PEt_3)_2$ [25], $PtH(NO_3)(PEt_3)_2$ [26], $PtCl_2$(1,4-bis(diphenylphosphino)butane) [27] were synthesised as described in the literature. $SnCl_2 \cdot H_2O$ was purchased from Fluka. Phenylacetylene (Aldrich) was distilled before use.

The carbonylation apparatus consists of a magnetically stirred 150 ml stainless steel autoclave equipped with valves and manometer. In a typical experiment, phenylacetylene (10 mmol) was placed in the autoclave together with the solvent (10 ml), the platinum catalyst (0.05 mmol), methanol (20 mmol) and if necessary $SnCl_2$. The reactor was purged with nitrogen, pressurised with CO and heated in a thermostated bath (± 0.1°C). After the desired reaction time, the reactor was cooled to room temperature, the residual gas removed and the reaction mixture analyzed by GLC using *p*-xylene as internal standard.

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References

[1] C. Botteghi, S. Paganelli, A. Schionato and M. Marchetti, Chirality, 3 (1991) 355.
[2] J.P. Rieu, A. Boucherle, H. Cousse and G. Mouzin, Tetrahedron, 42 (1986) 4095.
[3] A.S.C. Chan, Chemtech., March (1993) p. 47.
[4] S.C. Stinson, Chem. Eng. News, September 28 (1992) 46.
[5] P. Pino and G. Braca, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. II, Wiley, New York, 1977, p. 419–515.
[6] A. Mullen, in J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer Verlag, Berlin, 1980, Chap. 3.
[7] E. Drent, P. Arnoldy and P.H.M. Budzelaar, J. Organomet. Chem., 455 (1993) 247.
[8] J.F. Knifton, J. Mol. Catal., 2 (1977) 293.
[9] Y. Tsuji, T. Kondo and Y. Watanabe, J. Mol. Catal., 40 (1987) 295.
[10] A. Scrivanti, R. Chinellato and U. Matteoli, J. Mol. Catal., 84 (1993) L141.
[11] T. Masuda, N. Sasaki and T. Higashimura, Macromolecules, 8 (1975) 717.
[12] T. Masuda, T. Mouri and T. Higashimura, Bull. Chem. Soc. Jpn., 53 (1980) 1152.
[13] A. Furlani, I. Collamati and G. Sartori, J. Organomet. Chem., 17 (1969) 463.
[14] T.G. Appleton, H.C. Clark and R.J. Puddephatt, Inorg. Chem., 2 (1972) 2074.
[15] G. Odian, Principles of Polymerization, J. Wiley and Sons, New York, 1991, Chap. 3.4.
[16] T. Hayashi, M. Tanaka, Y. Ikeda and I. Ogata, Bull. Chem. Soc. Jpn., 52 (1979) 2605.
[17] D.A. Harbourne and F.G.A. Stone, J. Chem. Soc. A, (1968) 1765.
[18] T. Tohda, K. Sonogashira and N. Hagihara, J. Organomet. Chem., 110 (1976) C53.
[19] H.C. Clark, C.R. Jablonski and C.S. Wong, Inorg. Chem., 14 (1975) 1332.
[20] T.G. Attig, H.C. Clark and C.S. Wong, Can. J. Chem., 55 (1977) 189.
[21] D. Milstein, Acc. Chem. Res., 21 (1988) 428.
[22] P.J. Stang, Z. Zhong and A.M. Arif, Organometallics, 11 (1992) 1017.
[23] P.J. Stang and Z. Zhong, Organometallics, 11 (1992) 1026.
[24] J.C. Bailar and H. Itatani, Inorg. Chem., 4 (1965) 1618.
[25] G.W. Parshall, Inorg. Synth., 12 (1970) 26.
[26] J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
[27] A. Scrivanti, R. Campostrini and G. Carturan, Inorg. Chim. Acta, 142 (1988) 187.