Stoicheiometric Dimerisation of Methyl Acrylate mediated by $Pd(acac)_2$·HBF_4 Systems and its Relevance to the Mechanism of Catalytic Dimerisation of Acrylates (Hacac = $MeCOCH_2COMe$)

Isabelle Guibert, Denis Neibecker, and Igor Tkatchenko*

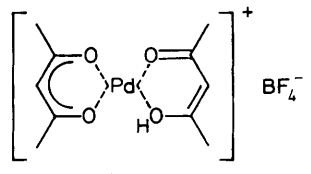
Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex, France

Protonation of $Pd(acac)_2$ (Hacac = $MeCOCH_2COMe$) by HBF_4·OEt_2 leads to ionic $[Pd(acac)S_2][BF_4]$ complexes, isolated for S = MeCN, which react with methyl acrylate to give selectively linear dimers *via* a palladium(IV) metallocycle.

We recently proposed new catalytic systems for the dimerisation of acrylates based on zero- or di-valent palladium complexes, phosphines, and excess HBF_4·OEt_2.[1] ^{31}P NMR monitoring of the model system {$Pd(acac)_2$, PBu_3, HBF_4·OEt_2} (Hacac = $MeCOCH_2COMe$) indicated that no hydridopalladium species stabilized by tributylphosphine were present in sufficient amounts (*e.g.* ≥5%) for detection. In fact, the protons added are trapped in the ions (**1**) (mainly) and (**2**).[2] In order to understand the mechanism of this transformation, we examined the reaction of HBF_4·OEt_2 with $Pd(acac)_2$ and its behaviour in the presence of methyl acrylate. We found that cationic palladium(II) species are involved in the catalytic process.

$[HPBu_3]^+$ (**1**)

$Bu_3\overset{+}{P}$–CH_2–CH_2–CO_2Me (**2**)



(**3**)

Addition of an equimolar amount of HBF_4·OEt_2 to $Pd(acac)_2$ in dichloromethane gives rise to the precipitation of a yellow–orange complex (79% yield). The elemental analysis agrees with the formula $Pd(acac)_2$·HBF_4. The ^1H and ^{13}C NMR shows the existence of an equilibrium between the *O*-protonated and the non-protonated forms (equation 1) which leads roughly to an equal amount of each species {^1H

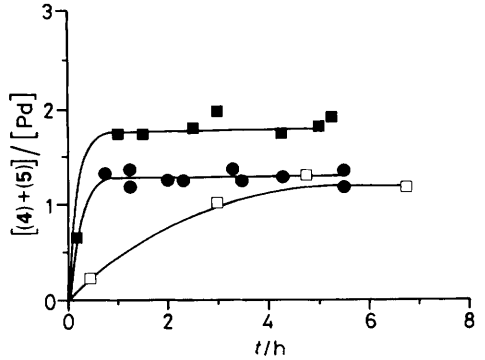
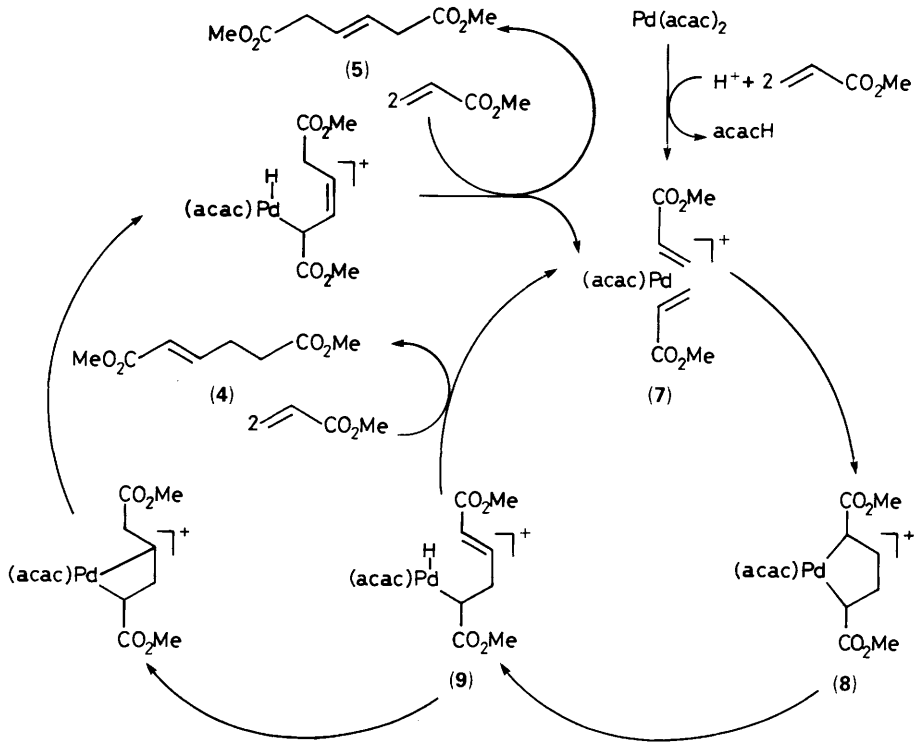
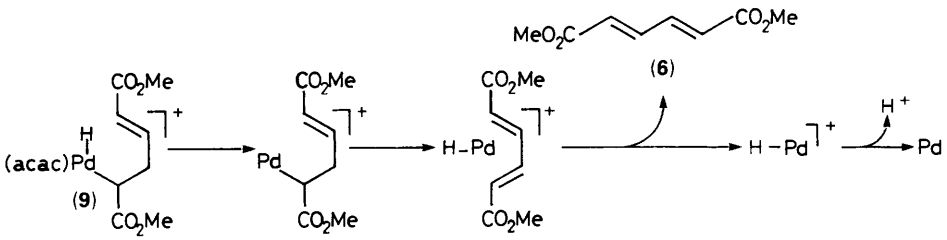


Figure 1. Conversion of methyl acrylate *vs.* time for different catalytic systems as referred to in Table 1 [■ $Pd(acac)_2/H^+$ (1:1); □ $Pd(acac)_2$·HBF_4; ● $Pd(acac)_2/H^+$ (1:2) or $Pd(acac)_2$·HBF_4/H^+ (1:1)].



Scheme 1



Scheme 2

NMR [200.13 MHz, $(CD_3)_2CO$]: δ 2.10 (s, 12H), 2.16 (s, 6H), 2.44 (s, 6H), 5.63 (s, 2H), 5.83 (s, 1H), 6.42 (s, 1H); ^{13}C NMR [50.32 MHz, $(CD_3)_2CO$, tetramethylsilane (TMS)]: δ 23.1 (q, $^1J_{CH}$ 129 Hz), 24.4 (q, $^1J_{CH}$ 130 Hz), 100.9 (d, $^1J_{CH}$ 162 Hz), 101.8 (d, $^1J_{CH}$ 165 Hz), 187.2 (s), 187.3 (s)} . Moreover these data associated with the IR results [nujol, 3450 (ν_{OH}), 1620 (ν_{CO}), 1570—1530 cm^{-1} (enol)] suggest that one ligand is an acetylacetone which is present in the enol form [reported ^{13}C values: δ 24.7 (Me, q, $^1J_{CH}$ 127 Hz), 100.3 (CH, d, $^1J_{CH}$ 164 Hz), 191.1 (CO, s)] rather than in the ketone form [δ 30.8 (Me, q, $^1J_{CH}$ 127 Hz), 58.5 (CH_2, t, $^1J_{CH}$ 129 Hz), 201.9 (CO, s)].

$$Pd(acac)_2 \cdot HBF_4 + (CD_3)_2CO \rightleftharpoons Pd(acac)_2 + (CD_3)_2CO \cdot HBF_4 \quad (1)$$

These data allow us to propose that the new complex formed under protonation of $Pd(acac)_2$ has the structure (**3**). If the protonation of $Pd(acac)_2$ is performed in tetrahydrofuran (THF), 0.9 equiv. (GC) of free acetylacetone is formed. The same behaviour is observed in acetonitrile: 0.84 equiv. of acetylacetone (GC) is obtained and a new complex, $[Pd(acac)(MeCN)_2][BF_4]$, could be recovered from the reaction mixture (67%; satisfactory elemental analysis was obtained). IR (CCl_4): 2330, 2310 (ν_{CN}), 1580—1520 cm^{-1} (ν_{CO} and ν_{CC}); ^1H NMR (90.02 MHz, CD_3CN, TMS): δ 2.14 (6H, acac), 2.00 (6H, broad peak arising from exchange between CD_3CN and MeCN), 6.27 (1H, acac); $^{13}C\{^1H\}$ (50.32 MHz, CD_2Cl_2, TMS) δ 3.6 (MeCN), 24.0 (MeCO), 100.7 (CH), 121.9 (CN), 186.5 (CO).

Reacting (**3**) (0.4 mmol) with a large excess of methyl acrylate (60 mmol) at 20 °C for 5 h leads to the formation of the expected dimers (**4**), (**5**) and a product which has been identified as dimethyl muconate (**6**) (Table 1). Furthermore, the reaction produces one equivalent of acetylacetone per palladium.

Better results are obtained if additional $HBF_4 \cdot OEt_2$ is added to (**3**) or if the protonation of $Pd(acac)_2$ is performed *in situ* (Table 1). The most efficient system corresponds to a 1 : 1 mixture of both these components as judged from the initial conversion rates (Table 1, Figure 1). The low catalytic activities observed (*e.g.* 1.3 to 1.9 turn-over) may arise from the low temperature used for the reaction and/or from the lack of stability of the palladium active species. Increase in temperature leads to polymerisation of methyl acrylate therefore preventing any further studies at higher temperatures.

No reaction occurs with methyl methacrylate. By contrast,

Table 1. Conversion of methyl acrylate with different systems made up from $Pd(acac)_2$ and $HBF_4 \cdot OEt_2$ {reaction conditions: $Pd(acac)_2$ (0.4 mmol), methyl acrylate (60 mmol), T = 20 °C, t = 6 h; yield corresponds to the ratio of the amounts of products formed to the amount of palladium salt engaged}.

System	H^+ [a]	H^+/Pd	Yield (4 + 5) /%	Selectivity (4) /%	Yield (6) /%
$Pd(acac)_2$	1	1	190	89	N.d.[b]
$Pd(acac)_2$	1	1	180	94	6
$Pd(acac)_2 \cdot HBF_4$	1	2	130	88	N.d.
$Pd(acac)_2 \cdot HBF_4$	3	4	130	86	N.d.
$Pd(acac)_2$	2	2	130	93	N.d.
$Pd(acac)_2 \cdot HBF_4$	0	1	130	87	N.d.
$[Pd(MeCN)_2(acac)]BF_4$	0	0	60[c]	81	N.d.

[a] H^+ added (equiv.). [b] N.d. = not determined. [c] t = 24 h.

co-dimerisation of methyl acrylate and methyl methacrylate does proceed albeit with a very low selectivity. The major products are dimers (**4**) and (**5**). These results indicate that the co-ordination of methyl methacrylate through its C=C bond is not favoured and suggest that the mechanism *via* C–H bond activation proposed by Oehme[3] does not take place for this type of catalyst.

We propose that on protonation one acetylacetonate ligand is removed from the co-ordination sphere of palladium (equation 2), therefore allowing the co-ordination of two methyl acrylate units as suggested from the isolation of $[Pd(acac)(MeCN)_2]BF_4$. This process has been already observed during kinetic studies[4] and in the preparation of some $[Pd(acac)L_2]BF_4$ complexes by protonation of $Pd(acac)_2$ generated *in situ* from $[Ph_3C]BF_4$ followed by addition of L.[5]

$$Pd(acac)_2 + HBF_4 \overset{n\mathrm{S}}{\rightleftharpoons} [Pd(acac)S_n]BF_4 + acacH \quad (2)$$

According to Scheme 1, (**7**) may undergo cyclometallation leading to the intermediate (**8**) which could be considered as a palladium(IV) complex. Such species have been already mentioned in oxidative addition processes.[6] Moreover organometallic Pd^{IV} compounds have been recently isolated[7] and proposed as reactive intermediates[8,9] in C–C bond formation reactions. The cyclometallation process is favoured on the basis of the isolation by Grevels *et al.* of bis(methyl acrylate)tricarbonyl iron complexes and the corresponding metallacycles.[10] It is worthy of note that only tail-to-tail coupling occurs. Although this selectivity may arise from steric hindrance, the interaction of the carbonyl moieties of the methyl acrylate with the electrophilic palladium centre may also lock the methyl acrylate ligands in the proper position for this coupling process. Formation of (**4**) as the major isomer is explained by β-elimination/reductive coupling processes (Scheme 1). The formation of (**6**) may occur from (**9**) (Scheme 2), but further work is needed in order to clarify this point.

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