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Coordinated Olefins as Incipient Carbocations: Catalytic Codimerization of Ethylene and Internal Olefins by a Dicationic Pt(II)−Ethylene Complex

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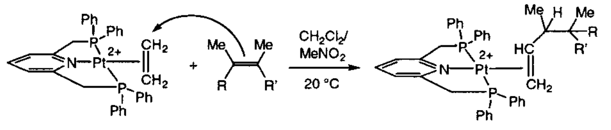
The nucleophilic addition reaction at Pd(II)[1] or Pt(II)[2] coordinated alkenes has been widely studied because of the great importance for the transformation or functionalization of hydrocarbons.[1,2] An important fact which has been revealed experimentally[3] and theoretically[4] is that the electrophilicity of the coordinated alkene can be enhanced by increasing the positive charge on the metal ion. A pictorial way to account for the reactivity enhancement is to look at the olefin (which during the nucleophile approach is slipping along its axis into an η^1 coordination mode[4,5]) as a metal-stabilized incipient carbocation (**A**), whose stability and fractional charge would increase with increasing positive charge on the metal ion. Accordingly, positively charged Pt(II) and Pd(II) complexes have been occasionally reported to promote carbocationic reactivity of alkenes,[6] such as ionic oligomerization[7] and polymerization[8] reactions, and, more recently, numerous catalyzed cyclizations of diynes and enynes.[9] Metal-stabilized carbocations have also been proposed as initiators for the polymerization of electron-rich monomers by $[Cp^*TiMe_2]^+$.[10] In no case, however, has a reaction between an olefin complex and a free alkene been observed, giving an isolable complex of the dimeric olefin.

We have recently described the first class of dicationic Pd(II)[11] and Pt(II)[12] complexes of simple monoalkenes, showing that their reactivity toward oxygen or nitrogen nucleophiles is increased (both kinetically and thermodynamically) by several orders of magnitude in comparison to neutral or monocationic species.[11b,12] We now report that the ethylene complex **1** (eq 1) can react also with moderately electron-rich alkenes, giving rise to a coupling reaction which turns into a nicely selective catalytic process.[13]



(1)

1 **2a-c**

(a) R = R' = H; **(b)** R = H, R' = Me; **(c)** R = R' = Me

In an initial experiment, when the isolated complex **1** (fluoroborate salt)[12] was reacted with the stoichiometric amount of the trisubstituted olefin 2-methyl-2-butene in $CH_2Cl_2/MeNO_2$ solution (10/1), a clean reaction took place in a few minutes at room temperature, giving the complex **2b** in nearly quantitative yield (eq 1). The product was obtained as an equimolar mixture of two diastereomeric pairs, differing by the relative configurations of the C(3) carbon atom and of the coordinated olefinic diastereoface.[14]

Complexes of propene and 1-butene were surprisingly not reactive. While the lack of reactivity of α-olefins higher than ethylene can be a limit to the scope of the reaction, on the other hand it is beneficial in that it precludes a successive oligomerization. In the presence of an excess of the substrates, it is therefore possible to achieve a selective catalytic process, via displacement of the coordinated product by free ethylene and further reaction. The reaction appeared to be very selective when run in $CH_2Cl_2/MeNO_2$, 10/1, at a catalyst concentration of 0.01 mol/L, forming the codimerization product 3,4-dimethyl-1-pentene almost exclusively. In plain nitromethane and high concentration of the catalyst the reaction rate was higher,[15] but ca. 10% of the homodimer 2,3,4,4-tetramethyl-1-hexene was formed.

The latter decene product was also rapidly formed (without any codimerization product) in a "blank" reaction run in absence of **1** but in the presence of etherated HBF_4 (0.1 mol %) as a catalyst. Therefore, the formation of the decene byproduct in the Pt-catalyzed reaction is very likely to be promoted by small amounts of acidic species formed upon degradation of the catalyst.[16]

The catalytic codimerization was comparably efficient with $Me_2C{=}CMe_2$ as substrate (giving 3,4,4-trimethyl-1-pentene), but much slower (ca. 5 ton in 24 h) with *Z*-2-butene (giving 3-methyl-1-pentene). The geminally disubstituted olefin 2-methyl-1-butene also gave the codimer 3,4-dimethyl-1-pentene. By monitoring the latter reaction by ^1H NMR we could observe the rapid formation of a small amount of the internal isomer 2-methyl-2-butene, whose concentration, however, remained small and approximately stationary while the codimerization proceeded. This indicates that complex **1** is able to catalyze the interconversion between the two isomeric pentenes, but since their equilibrium ratio would be largely in favor of 2-methyl-2-butene,[17] it also indicates that the latter was the reacting species, selectively consumed by the successive reaction with **1** (eq 1) at the same overall rate of its production. Isobutylene did not give any hydrovinylation product, being instead dimerized mainly to $CH_2{=}C(Me)CH_2CMe_3$, most likely via an acid-catalyzed pathway like that leading to the decene homodimer of 2-methyl-2-butene (see above).

Although the catalytic runs were performed using "anhydrous" solvents, we could not exclude the presence of traces of water in the system. However, when water was deliberately added to the solution (1 mol/mol catalyst), the effect on the substrate conversion was deleterious, confirming the initial assumption (eq 1) that the reaction takes place via direct activation of ethylene by coordination to the doubly positive metal center.[18]

To get further mechanistic insight, we performed the reactions with C_2D_4. In all the cases one deuterium atom was selectively transferred from the ethylene molecule to the adjacent C(3) carbon atom of the product $CD_2{=}CD{-}CD(Me)C(Me)RR'$, while the vinyl group retained its original deuterium content. A proposed mechanism for the catalytic cycle is shown in Scheme 1.

The carbocation (**B**) generated from the nucleophilic attack on the "slipping" coordinated ethylene (**A**) could in principle react along various paths, among which the capture of the R group is

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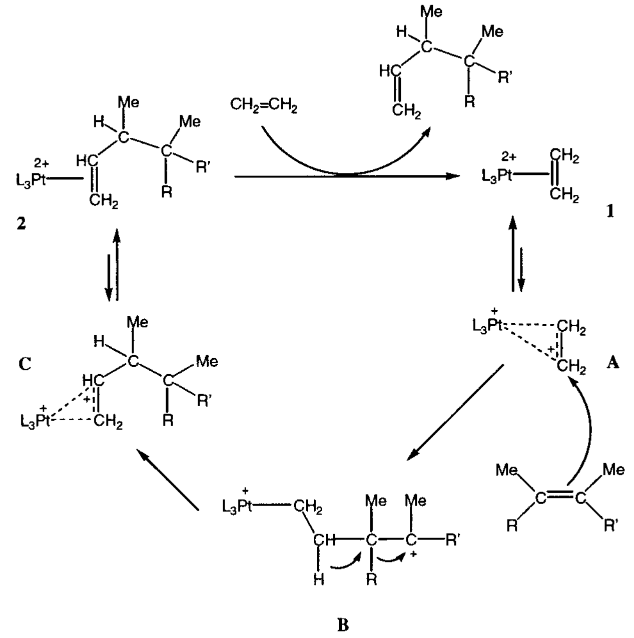
Scheme 1



reasonably preferred since it produces a carbocation at least as stable as **B**.[19] At this point the capture of a vicinal hydride to form the delocalized cation **C**, with final slipping to the ground-state product **2**, is the expected downhill evolution of the system. The final displacement of the coordinated olefinic product giving back the starting complex **1** is straightforward, being thermodynamically favored ($K_{eq} = 4 \pm 1$, as determined by ^{1}H NMR on the isolated complexes **2**) and kinetically smooth (half-life 1−2 min under the conditions of the catalytic reaction).

In the above mechanism the Pt^{2+} ion plays the double role of activating the ethylene molecule in the transition state **A** and stabilizing the transition state **C**, thereby reducing the occurrence of possible side reactions of the carbocation **B**. The latter are most likely responsible for the deactivation of the catalyst, accompanied by the release of protons[16] and the formation of stable[11] and unreactive Pt−C σ-bonded species.[15] The mechanism in Scheme 1 is also consistent with the failure of isobutylene to give an hydrovinylation product, since the first step in the evolution of **B** (the capture of R = H) would produce a secondary carbocation and thus be disfavored. Acid-catalyzed homodimerization was therefore the prevailing reaction.

Although many issues need to be addressed by further experiments (including the very existence of the postulated intermediate **B** and the possible role of solvent and counterion), our results have shown that ethylene, when coordinated to a highly electrophilic metal center, displays a carbocationic reactivity that gives rise to a catalytic hydrovinylation process. This newly found reaction appears to be alternative or complementary to known metal-catalyzed codimerizations occurring through different pathways.[13] Its scope and potentiality are currently under investigation.

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(13) Although the metal-catalyzed hydrovinylation of olefins is known by far (for a leading reference, see: Jolly, P. W.; Wilke, G. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 2, pp 1024−1048), the known cases appear to involve insertion−elimination steps into M−H bonds rather than direct attack of an external olefin on a coordinated double bond, which seems to be unprecedented (see also Nomura, N.; Jin, J.; Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 459 and references therein).

(14) Crystallized from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3NO_2): diastereomer **2b′** δ 0.33 (d, 3H, CH_3), 0.36 (d, 3H, CH_3), 0.52 (d, 3H, CH_3), 1.55 (m, 1H, CH), 1.74, (m, 1H, CH), 4.24 (1H, m, =C*H*H), 4.52 (1H, m, =CH*H*), 4.75 (d ps t, 2H, PCH_aH_b), 5.07 (d ps t, 2H, PCH_aH_b), 5.4 (m, 1H, =CH), 7.6−8.0 (m, 22H, Ph, py), 8.08 (t, 1H, py). Diastereomer **2b″** δ 0.40 (d, 3H, CH_3), 0.43 (d, 3H, CH_3), 0.90 (d, 3H, CH_3), 1.18 (m, 1H, CH), 1.85, (m, 1H, CH), 4.42 (1H, m, =C*H*H), 4.56 (1H, m, =CH*H*), 4.66 (d ps.t, 2H, PCH_aH_b), 5.15 (br m, 2H, PCH_aH_b), 5.4 (m, 1H, =CH), 7.6−8.0 (m, 22H, Ph, py), 8.16 (t, 1H, py). Anal. Calcd for $C_{38}H_{41}B_2F_8NP_2Pt$: C, 48.43; H, 4.38; N, 1.49. Found: C, 48.17; H, 4.49; N, 1.65.

(15) Unoptimized conditions: a mixture of **1** (87 mg, 0.10 mmol), anhydrous $MeNO_2$ (1.0 mL, free from nitriles), 2-methyl-2-butene (3.2 mL, 30 mmol), giving two liquid phases, was stirred at 20 °C under ethylene at atmospheric pressure. The reaction was monitored (^{1}H NMR) by repeated sampling (10-μL portions) of the upper hydrocarbon phase. After 7 h (85% conversion), the upper layer was collected and the main product separated by fractional distillation (3,4-dimethyl-1-pentene, 1.9 g, 65% yield based on 2-methyl-2-butene). The lower layer (nitromethane phase) was evaporated to dryness and the solid residue analyzed by ^{1}H and ^{13}C NMR spectroscopy. The major component of the residue (ca. 40% of the total) was identified as complex **2b**. Although the second component (ca. 30% of the total) was not identified, it was inferred to be a σ-bonded derivative by a peak in the ^{13}C NMR spectrum at $\delta = -4.9$, flanked by ^{195}Pt satellites ($^1J_{C-Pt} = 625$ Hz).

(16) In one experiment, the catalytic reaction was run in CD_3NO_2 and directly monitored by ^{1}H NMR. A broad signal (due to traces of water) was detectable, which slowly moved downfield (in the range 2−4 ppm), suggesting a progressive protonation by slow degradation of the catalyst.

(17) The catalytic isomerization reaction was separately monitored by ^{1}H NMR, after adding a large excess (20 equiv) of 2-methyl-1-butene to an NMR sample of **1**. After 1 h at room temperature, a 90% conversion to the internal isomer 2-methyl-2-butene was observed.

(18) We can therefore exclude that water might interact with the metal ion and promote the formation of carbocationic active species by acting as a Brønsted acid.[8,10]

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