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Catalytic Coupling of Ethylene and Internal Olefins by Dicationic Palladium(II) and Platinum(II) Complexes: Switching from Hydrovinylation to Cyclopropane Ring Formation

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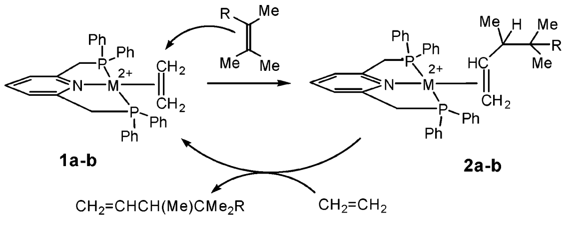
*Summary: The dicationic palladium(II) and platinum(II) complexes [(PNP)M(C_2H_4)](BF_4)$_2$ (**1a**, M = Pt; **1b**, M = Pd; PNP = 2,6-bis((diphenylphosphino)methyl)pyridine) and [(PPP)Pt(C_2H_4)](BF_4)$_2$ (**7**; PPP = triphos) catalyze a cross-coupling reaction of ethylene with tri- and tetrasubstituted olefins, which can lead to both hydrovinylation and cyclopropanation products. The product ratio is strongly affected by the choice of the ligand and of the metal, the two limiting cases being **1a** and **7**, which selectively give the hydrovinylation and the cyclopropanation products, respectively.*

The electrophilic activation of unsaturated substrates by coordination to a transition-metal ion is a very remarkable phenomenon, which is found at the core of most relevant metal-catalyzed processes.[1] An important fact which has been revealed experimentally[2] and theoretically[3] is that the electrophilicity of the coordinated alkene can be enhanced by increasing the positive charge on the metal ion. With the aim of exploiting this concept, we recently prepared the first class of dicationic Pd(II)[4] and Pt(II)[5] monoalkene complexes, which revealed a new and somehow unexpected reactivity. Indeed, the platinum−ethylene complex **1a** was found to react with tri or tetrasubstituted alkenes, giving rise to an unprecedented[6] catalytic hydrovinylation process (eq 1).[7]

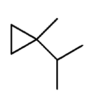


(1)

(**a**) M = Pt; (**b**) M = Pd;   R = H, Me

As a natural extension of this study, we began to examine the analogous Pd(II) system, and to our surprise we observed, in addition to the reaction shown in eq 1, the competitive formation of a cyclopropane derivative. Since three-membered rings are important and challenging targets,[8] the latter reaction appeared to be worthy of particular attention, because it represents an example of a potentially general new way to their construction.[9]

Unlike the case of the platinum complex **1a**,[7] the stoichiometric (1:1) reaction of **1b** (fluoroborate salt) with 2-methyl-2-butene was sluggish and did not lead to a clean isolable compound. However, when **1b** was reacted at 20 °C with 4 equiv of the same olefin in $MeNO_2$ saturated with ethylene, the complex **2b** (R = H) was obtained almost quantitatively after flash distillation of the solvent,[10] while the distillate mainly contained an hydrocarbon product which was identified by ^1H and ^{13}C NMR as 1-methyl-1-isopropylcyclopropane (**3**), plus some hydrovinylation product **3′** and small amounts of the decene **4**. 1-Methylcyclohexene and the tetrasubstituted olefin $Me_2C{=}CMe_2$ behaved similarly, giving **5** and **6**, respectively, as cyclopropane derivatives.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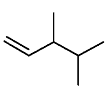
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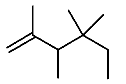
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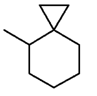
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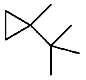
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No reaction was obtained by using the less substituted olefin (*Z*)-2-butene as substrate, while isobutylene mainly gave homodimers as in the case of platinum.[7] Replacing ethylene with propene gave no reaction. The influence

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[1] Crabtree, R. H. *The Organometallic Chemistry of Transition Metals,* 3rd ed.; Wiley: New York, 2001.

[2] (a) Maresca, L.; Natile, G.; Rizzardi, G. *Inorg. Chim. Acta* **1980**, *38*, 53. (b) Annibale, G.; Maresca, L.; Natile, G.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1587. (c) Maresca, L.; Natile, G. *Comments Inorg. Chem.* **1994**, *16*, 95 and references therein.

[3] (a) Sasaki, S.; Maruta, K.; Ohkubo, K. *Inorg. Chem.* **1987**, *26*, 2499. (b) Strömberg, S.; Svensson, M.; Zetterberg, K. *Organometallics* **1997**, *16*, 3165.

[4] (a) Hahn, C.; Vitagliano, A.; Giordano, F.; Taube, R. *Organometallics* **1998**, *17*, 2060. (b) Hahn, C.; Morvillo, P.; Vitagliano, A. *Eur. J. Inorg. Chem.* **2001**, 419.

[5] Hahn, C.; Morvillo, P.; Herdtweck, E.; Vitagliano, A. *Organometallics* **2002**, *21*, 1807.

[6] Although the metal-catalyzed hydrovinylation of olefins is known (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).

[7] Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038.

[8] Salaun, J. *Top. Curr. Chem.* **2000**, *207*, 1.

[9] Methods for the synthesis of cyclopropanes have been reviewed. See: Ohkita, M. Nishida, S. Tsuji, T. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1995; pp 261−318. Tsuji, T.; Nishida, S. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; pp 308−373.

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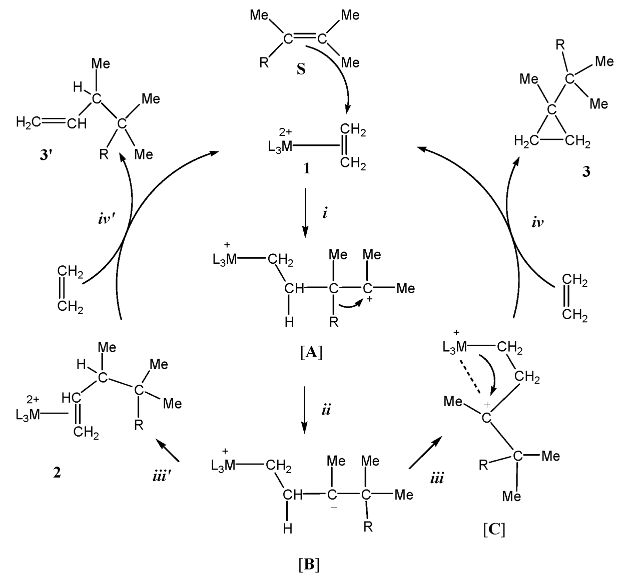
Table 1. Yield and Product Distribution in the Reaction of Ethylene with 2-Methyl-2-butene under Various Conditions[a]

entry	catalyst, solvent	*T* (°C)	*t* (h)	*p* (bar)	reacted substrate (%)	product distribn (mol %)		
						3	**3′**	**4**
1	**1b**,[b] CH_2Cl_2	20	24	1	18	37	57	6
2	**1b**, $MeNO_2$	20	4	1	16	54	32	14
3		20	24	1	52	54	31	15
4		0	24	1	8	70	24	6
5		20	4	6	60	63	31	6
6		20	24	6	97	63	31	6
7		0	4	6	16	72	35	3
8	**1a**, $MeNO_2$	20	4	6	95	0[c]	95	5
9	**7**,[d] $MeNO_2$	20	48	6	11	100	0	0
10		60	48	6	28	90	7	3

[a] Concentration of the catalyst before addition of the substrate: 0.10 M (0.33 mol % of the added substrate). [b] Solvent containing 20% $MeNO_2$; initial concentration of the catalyst (1 mol %) 0.02 M. [c] 100% **3′**, **3** detectable in traces (<0.4%). [d] **7** = $[(triphos)Pt(C_2H_4)](BF_4)_2$.

Scheme 1



of the reaction conditions on the substrate conversion and product distribution was examined in the case of 2-methyl-2-butene, using a constant ethylene pressure and a large excess (300 equiv) of the substrate (see Table 1).[11]

In the experiments summarized in Table 1, a relatively low amount of catalyst (0.33 mol %) was purposely used, to allow homogeneous comparisons between different conditions. Using a larger percentage of catalyst, a proportionally larger percent conversion of the substrate was obtained. For example, by repeating the experiment in entry 9 using 2 mol % of catalyst **7**, a 60% conversion of the substrate was obtained. By inspection of Table 1 it appears that both the reaction rate and the fraction of the cyclopropane product **3** increase with the polarity of the solvent, which, however, produces a larger fraction of the byproduct **4**.[12] Lowering the temperature is beneficial for the selectivity but obviously decreases the reaction rate. Both the reaction rate and the selectivity increase with the ethylene pressure. In an attempt to further improve the selectivity, we changed the ligand, first aiming at a triphos palladium complex analogous to **1b** (triphos = bis(2-(diphenylphosphino)ethyl)phenylphosphine). After a couple of unsuccessful trials we shifted to platinum and we could obtain the complex $[(triphos)Pt(C_2H_4)](BF_4)_2$ (**7**).[13] This turned out to be a very selective catalyst for the production of the cyclopropane derivative **3**, although its activity was much lower than that of the corresponding PNP complex **1a**. We also explored the effect of the counterion, by replacing BF_4^- with $B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4^-$, without any substantial effect on the rate and selectivity.

A mechanism accounting for both reaction pathways and partially explaining the observed trends is proposed in Scheme 1. The hydrovinylation pathway (left portion of Scheme 1), occurring through the intermediates **A** and **B**,[14] has been already proposed by us in a previous paper.[7] In an alternate path, an attack of the carbocation **B** on the M−C σ-bond (possibly mediated by the metal in an intermediate **C**) can give (steps ***iii*** and ***iv***) the cyclopropane derivative **3**. Related examples of intramolecular C−C bond formation reactions resulting from the attack of a π-carbon nucleophile on a cationic π-complex have recently been reported.[15] It is interesting to note that a mechanistically very similar process (also displaying similar selectivities) has been quite recently observed by Gagné and co-workers in Pt^{2+}- and Pd^{2+}-mediated cycloisomerization reactions of 1,6-dienes.[16]

In the case of the Pt(PNP) complex **1a** the above mechanism is supported by the NMR detection in the reaction residue of two σ-bonded species, identified

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[10] Crude mixture of two diastereomers, washed with Et_2O and dried. ^1H NMR (300 MHz, CD_2Cl_2): diastereomer **2b′** δ 0.39 (d, 3H, CH_3), 0.54 (d, 3H, CH_3), 0.97 (d, 3H, CH_3), 1.24 (m, 1H, CH), 2.01, (m, 1H, CH), 4.39 (d ps t, 2H, PCH_aH_b), 4.95 (m, 2H, $=CH_2$), 5.39 (d ps t, 2H, PCH_aH_b), 5.90 (m, 1H, =CH), 7.6−8.0 (m, 23H, Ph, py); diastereomer **2b″** δ 0.43 (d, 3H, CH_3), 0.45 (d, 3H, CH_3), 0.99 (d, 3H, CH_3), 1.16 (m, 1H, CH), 1.96, (m, 1H, CH), 4.19 (d ps t, 1H, =CHH), 4.61 (d ps t, 2H, PCH_aH_b), 4.75 (1H, d, =CHH), 5.23 (d ps t, 2H, PCH_aH_b), 5.68 (m, 1H, =CH), 7.6−8.0 (m, 23H, Ph, py). The analytical sample was obtained by displacing ethylene from complex **1b** at reflux in CH_2Cl_2 with an excess of **3**, followed by crystallization with pentane. Anal. Calcd for $C_{38}H_{41}B_2F_8NP_2Pd$: C, 53.46; H, 4.84; N, 1.64. Found C, 53.10; H, 4.61; N, 1.51.

[11] A most effective solvent proved to be nitromethane (free from nitriles). Under typical reaction conditions (1 mL of CH_3NO_2, 0.1 mmol of catalyst, 3 mL of substrate) this solvent has the advantage of giving a double-phase system, in which the catalyst works in the nitromethane phase and the products are extracted in the upper hydrocarbon layer. Weakly coordinating solvents such as acetone and propylene carbonate strongly inhibit the reaction.

[12] As in the case of platinum,[7] the dimerization of 2-methyl-2-butene, producing **4**, is most likely due to a Brønsted acid catalysis by acidic species generated upon hydrolysis or degradation of the catalyst.

[13] The compound (**7**) was prepared from commercial triphos as described for **1a**.[5] The coordinated ethylene is weakly bound and is easily displaced, even by traces of water and by diethyl ether. Pentane was used for its precipitation from CH_2Cl_2. ^1H NMR (400 MHz, CD_3NO_2): δ 2.8−3.0 (m, 4H, PCH_2), 3.3−3.8 (m, 4H, PCH_2), 4.55 (s, 4H, $CH_2{=}CH_2$, J_{H-Pt} = 37 Hz), 7.5−8.0 (m, 25H, Ph). ^{13}C NMR (50 MHz, CD_3NO_2): δ 28.0 (m, $P-CH_2$), 32.7 (m, $P-CH_2$), 91.1 ($CH_2{=}CH_2$), 124.0 (P−C), 127.0 (P−C), 131.3, 131.4, 134.1, 135.0, 135.4, 136.4 (C_{Ph}). Due to the easy loss of ethylene by the compound, we could not obtain a satisfactory elemental analysis.

[14] In this mechanism, the tertiary carbocation **A** is initially formed in step ***i*** upon nucleophilic attack of the electron-rich substrate **S** on the coordinated ethylene molecule and rearranges in step ***ii*** to the comparably stable carbocation **B**. At this point, a further hydride shift can move the positive charge on the β-position, stabilized by the "slipping"[7] (step ***iii′***) into the olefin complex **2**, which by displacement gives (step ***iv′***) the hydrovinylation product **3′**.

[15] (a) Franzén, J.; Löfstedt, J.; Falk, J.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2003**, *125*, 14141. (b) Dorange, I.; Löfstedt, J.; Närhi, K. Franzén, J.; Bäckvall, J.-E. *Chem. Eur. J.* **2003**, *9*, 3445.

[16] Kerber, W. D.; Hwan Koh, J.; Gagné, M. R. *Org. Lett.* **2004**, *6*, 3013.

as (PNP)Pt$-CH_2CH_2C(Me){=}CMe_2$ (**D**) and (PNP)Pt$-CH_2CH_2C(Me_2)CH(Me)CH{=}CH_2$ (**E**). The first species (**D**) is likely to be generated from proton elimination (in the case of R = H) by the carbocation **A**; the second species (**E**) results from further reaction of the tetrasubstituted double bond in **D** with the coordinated ethylene molecule in **1a**.[17] However, in the case of the (PPP)Pt complex **7** no intermediates analogous to **D** and **E** could be detected in the reaction residue, which contained a predominant (>85%) species that regenerated the starting catalyst **7** upon addition of ethylene in nitromethane solution. Therefore, we do not have so far direct evidence of carbocations **A** and **B** being actually involved in the formation of the cyclopropane derivative **3**. Nevertheless, the proposed mechanism is consistent with the outcome of the reaction with C_2D_4 under the conditions of entry 3 in Table 1. In the product **3** (whose ratio to **3′** increased from 1.7 to 3.3 by a remarkable isotopic effect) the four D atoms were all found in the CD_2CD_2 moiety of the cyclopropane ring, while in **3′** one D atom was selectively transferred to the carbon adjacent to the vinylic group, which retained the remaining three D atoms. On the other hand, an alternative mechanism involving a possible alkylidene metal complex derived from 2-methyl-2-butene seems unlikely, since the product distribution in the "nearly stoichiometric" reaction was about the same as in the catalytic runs, although (the ethylene concentrations being the same in the two cases) the 2-methyl-2-butene concentration was far smaller in the former experiment.

Some of the observed trends easily fit within the proposed mechanism. Thus, the increase of the reaction rate with the solvent polarity is consistent with the involvement of carbocationic species, and the reduction of the byproduct **4** upon increasing the ethylene pressure or decreasing the temperature is consistent with the resulting increase of the population of the reactive species **1** vs the unreactive species **2**. However, the strong dependence of the product selectivity on the metal and the ligand (which is actually the most important observation) is not so straightforward. A possible but rather speculative explanation is that the barrier to step ***iii′*** might increase when the stability of the olefin complex **2** decreases (Pd vs Pt and PPP vs PNP),[18] thus favoring the competitive step ***iii*** and the cyclopropane ring formation.

In summary, coordination to a dicationic metal center activates ethylene toward a cross-coupling reaction with electron-rich tri- and tetrasubstituted olefins, which can be directed to form a hydrovinylation product or a cyclopropane derivative by switching the ligand and/or the metal ion. Whether or not this reaction might have a scope sufficient to become a useful synthetic tool is yet to be determined, although the mechanistically similar results recently reported by Gagné for some cycloisomerization reactions of 1,6-dienes[16] seem to indicate very promising developments. Future studies will be aimed at exploring such potentialities and at clarifying the mechanism, especially concerning the role of the metal in assisting the final ring-closure step.

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(17) To favor proton elimination from the postulated carbocation **A**, a small amount of water (7 μL) was added to the reaction mixture shortly after the addition of the substrate. After 1 h the nitromethane phase[11] was separated and dried in vacuo. The solid residue was treated with aqueous NaBr to displace any coordinated olefin, extracted with CH_2Cl_2, and dried again. ^1H NMR (300 MHz, CD_2Cl_2): **D** δ 1.02 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 4.42 (ps t, 4H, PCH_2); **E** δ 0.34 (s, 3H, CH_3), 0.36 (s, 3H, CH_3), 0.52 (d, 3H, $CHCH_3$), 1.64 (m, 1H, $CHCH_3$), 4.42 (app t, 4H, PCH_2), 4.64 (d, 1H, $=CH_EH_Z$), 4.68 (d, 1H, $=CH_EH_Z$), 5.38 (ddd, 1H, $=CH$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): **D** δ 0.0 (CH_2-Pt, $^1J_{C-Pt} = 635$ Hz), 17.7 (CH_3), 19.4 (CH_3), 20.5 (CH_3), 39.9 (CH_2), 46.4 (ps t, PCH_2); **E** δ -4.9 (CH_2-Pt, $^1J_{C-Pt} = 625$ Hz), 14.6 (CH_3), 23.4 (CH_3), 23.6 (CH_3), 37.2 (CH_2), 45.8 (ps t, PCH_2), 46.7 (CH), 113.7 ($=CH_2$), 142.3 ($=CH$).

(18) Palladium generally binds an olefin 12−15 kcal/mol more weakly than the corresponding Pt system.[3b] The Pt−olefin bond is also expected to be weaker in the PPP complex than in the PNP complex, due to the well-known larger trans influence of phosphorus compared to nitrogen. This is confirmed by the much lower stability of complex **7** vs **1a** to olefin substitution.[13]