Diastereoselective Alkylation−Vinylation of Norbornene Catalyzed by a Tetrahedral Cobalt(II) Pyridinimine Complex

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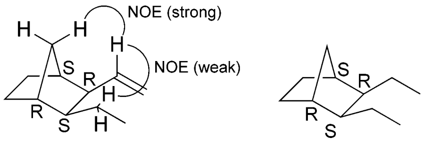
Summary: On activation by MAO the Co^{II} pyridinimine dichloride complex $CoCl_2N_2^{Ph}$ catalyzes the unprecedented enchainment of one norbornene molecule with two ethylene molecules to give exo-2,exo-3 ethyl-vinylnorbornane with high activity and complete diastereoselectivity.

On activation by methylaluminoxane (MAO), the Co^{II} pyridinimine complex $CoCl_2N_2^{Ph}$ (**1**; N_2^{Ph} = [1-(6-phenylpyridin-2-yl)ethylidene)](2,6-diisopropylphenyl)amine) is known to generate a very active and selective catalyst for the dimerization of ethylene (E) to 1-butene,[1] while α-olefins are converted to internal dimers.[2] We have now found that no catalytic polymerization/oligomerization reaction occurs with cyclic olefins such as norbornene (NB), whereas the ethylation−vinylation of the latter substrate takes place with high activity and complete diastereoselectivity on feeding the reactor with a mixture of E and NB. This new reaction, a Co^{II}-catalyzed 1:2 NB/E heterotrimerization, is herein described.

It has been recently demonstrated that the tetrahedral high-spin complex **1** reacts with MAO in toluene to give a low-spin Co^{II} square-planar methyl complex.[3] This species, intercepted by EPR spectroscopy, inserts E to form a cobalt−propyl intermediate that eliminates propene with formation of a Co−H initiator. The formation of this species is apparently inhibited by olefins unable to eliminate β-hydrogen such as NB, as demonstrated by the reaction A illustrated in Scheme 1 that, following acid hydrolysis, allowed for the stoichiometric synthesis of two new molecules, namely *exo*-2,*exo*-3(methylnorbornanyl)-bicyclo[2.2.1]heptane (**2**) and *exo*-2-methylbicyclo-[2.2.1]heptane (**3**).

In order to generate a Co−H moiety, the presence of E is therefore necessary. As a matter of fact, the concomitant presence of E and NB in the reactor led to an unprecedented heterotrimerization reaction, yielding *exo*-2,*exo*-3 ethyl-vinylnorbornane (**4**) in up to 97% selectivity (de > 99%) with TOFs as high as 270 000 mol of NB transformed (mol of Co)$^{-1}$ h^{-1} (Scheme 1, reaction B). Table 1 reports data for catalytic reactions performed at different E and NB concentrations. Notably, the plain hydrovinylation product **5**, which is commonly obtained by E/NB coupling by late-transition-metal catalysis,[4,5] and the new 1:3 NB/E adduct **6** were produced in very low amounts.[6] Moreover, the presence of NB in the feed almost completely suppressed the production of butenes (see the Supporting Information).



4 **7**

Figure 1.

Unequivocal identification of **4** as a single diastereomer in its racemic form was obtained by GC analysis and ^{1}H and ^{13}C NMR spectroscopy, including a 2D phase-sensitive NOESY experiment, as well as by the ^{13}C NMR spectrum of the hydrogenated form 2,3-diethylbicyclo[2.2.1]heptane (**7**), whose ^{13}C NMR spectrum showed two chemically and magnetically equivalent ethyl groups (Figure 1 and Table 2).[7]

Two different catalytic protocols, A and B, have been used to carry out the ethylation−vinylation of NB. Methods A and B differ from each other in the amount of the precatalyst (12 μmol vs 1.2 μmol) and in the reagent-addition sequence. In method A, precatalyst, activator, and NB were introduced into the reactor prior to pressurization with E, while in method B, the precatalyst was added after mixing all of the other reagents under the desired experimental conditions. Low temperatures and high E pressures favored the formation of **4** (entries 1−3 and 4, 8, 9), while high NB molar fractions increased the amount of the hydrovinylated product **5** (entries 4, 5, 6, and 8). It is therefore apparent that that the side product **5** was mostly produced at the initial stage of the process (entry 8 vs 7) when the NB molar fraction was high (entries 10 and 13). In all cases, the heterotrimerization process was best accomplished by using a very low catalyst loading at high E concentrations (entries 11−13).

Scheme 2 illustrates a reaction mechanism that might account for the observed chemo- and stereoselectivity. In the light of the product selectivity and of the established ability of **1**/MAO to catalyze the dimerization of E (Scheme 2, path **B**), as well

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[6] The exo stereochemistry for compounds **2**, **3**, **5**, and **6** was assigned on the basis of the diastereoselectivity of the ethylated−vinylated product **4**.

[7] The hydrogenation of **4** was carried out in CH_2Cl_2 using 1 mol % of the Wilkinson catalyst (room temperature, 1 bar of H_2, 3 h).

[8] For norbornene oligomers with a vinylic end group employed to prepare new polymeric materials see: Myagmarsuren, G.; Jeong, O. Y.; Ihm, S-K. *Appl. Catal. A: Gen.* **2004**, *275*, 271.

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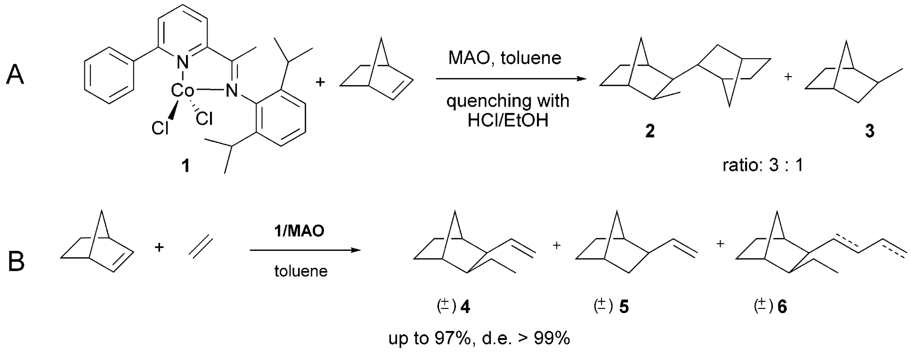
Table 1. Diastereoselective Alkylation−Vinylation of Norbornene Catalyzed by $CoCl_2N_2^{Ph}$ [a]

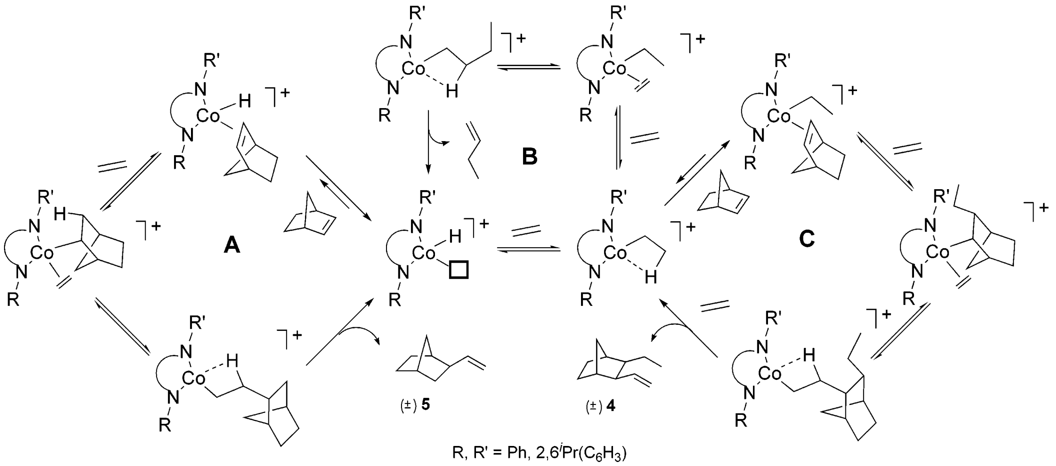
entry	t (°C)	T (min)	amt of Co^{Ph} (μmol)	method	P (bar)	[E][b]	[NB]	χ_{NB} [c]	NB conversn (%)[d]	TON[e]	**5**	**4**	**6**
1	−20	30	12	A	4	1.15	0.18	13.53	17.9	269	2.08	96.83	1.09
2	0	30	12	A	4	0.79	0.18	18.56	100	1500	3.03	96.11	0.86
3	0	20	12	A	8	1.58	0.18	10.23	100	1500	2.78	96.43	0.79
4	10	30	12	A	4	0.67	0.18	21.18	100	1500	3.06	95.90	1.04
5	10	30	12	A	4	0.67	0.35	34.31	100	2917	5.56	93.74	0.70
6	30	30	12	A	1	0.12	0.18	60.00	57.6	864	11.27	87.43	1.30
7	30	3	12	A	4	0.50	0.18	26.47	67.1	1007	8.84	90.32	0.84
8	30	30	12	A	4	0.50	0.18	26.47	100	1500	8.77	90.47	0.76
9	50	30	12	A	4	0.38	0.18	32.14	65.6	984	9.73	88.95	1.32
10	0	20	1.2	A[f]	8	1.58	0.35	18.13	100	29167	6.53	92.43	1.04
11	0	2	1.2	B	4	0.79	0.18	18.56	59.9	8985	2.97	96.38	0.65
12	0	10	1.2	B	4	0.79	0.18	18.56	100	15000	2.69	96.56	0.75
13	0	20	1.2	B	8	1.58	0.35	18.13	100	29167	2.95	96.51	0.54

[a] Conditions: all reactions in 100 mL of toluene, amount of co-cat MAO, 600 equiv (method A) and 3000 equiv (method B). [b] Calculated according to Henry's law: $C_E = P_E H_0 \exp[\Delta H_L(RT)^{-1}]$, C_E (mol L^{-1}), P_E (atm), $H_0 = 0.001\,75$ mol L^{-1} atm^{-1}, ΔH_L = enthalpy of solvation of E in toluene = 2569 cal mol^{-1}, $R = 1.989$ cal mol^{-1} K^{-1}. [c] $\{[NB]/([NB] + [E])\} \times 100$. [d] Determined by GC. [e] Calculated as mol of NB (mol of Co)$^{-1}$. [f] Method A except for using 1.2 μmol of the precatalyst and 3000 equiv of MAO.

Scheme 1



Scheme 2



as the independent reactivity of **1**/MAO with NB (Scheme 1, reaction A), there is little doubt that NB prevails over E for the insertion into the Co−ethyl bond (Scheme 2, paths **B** and **C**), while E prevails over NB for insertion into the Co−H bond (Scheme 2, paths **A** and **B**). This finding is in contrast with all previously reported hydrovinylation reactions of NB by late-transition-metal catalysis, essentially Ni−phosphine complexes,[4,5] where NB inserts selectively into M−H bonds.

Table 2. $^{13}C\{^1H\}$ NMR Parameters for 7 (100.62 MHz, 23 °C, $CDCl_3$)

nucleus	δ (ppm)	nucleus	δ (ppm)
CH_3^{Et}	14.28	$-CHCH_2CH-$	32.60
CH_2^{Et}	22.25	$-CHCH_2CH-$	40.27
$-CH_2CH_2-$	30.02	$-CHEt$	46.78

The chemical underpinnings to the insertion selectivity observed are the object of current studies, somewhat thwarted by the paramagnetic nature of both precursor and propagating alkyls. The situation is further complicated by the chelating pyridinimine ligand containing two electronically and sterically different N donor atoms that may control which atom (H or alkyl) is preferentially coordinated in either trans position. It is therefore likely that the ethylation−vinylation of NB is actually controlled by a complex web of electronic and steric factors. On the other hand, addressing this intriguing point would be of valuable importance to extend the applicability of the present reaction to other cyclic olefins and α-olefins and hence to a new class of functionalized vinyl monomers. Preliminary results show that bulky olefins such as dicyclopentadiene and norbornadienes are active substrates, whereas no reaction occurs with plain cyclic olefins such as cyclopentene, cyclohexene, and styrene. Moreover, there is evidence that both the activity and the selectivity of the alkylation−vinylation can be tuned by structural variations of the supporting pyridinimine ligand.[1,3]

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Supporting Information Available: Text and figures giving details of the E/NB heterotrimerization protocols, characterization data for compounds **4** and **7**, and ethylene consumption curves recorded for some selected experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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