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Highly Selective Synthesis of 4-Vinylcyclohexene by Cyclodimerization of Butadiene catalysed by Aminophosphinephosphinite and Bis(aminophosphine) Chiral Ligands Nickel Complexes

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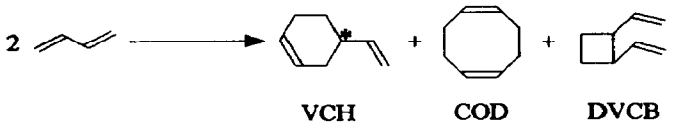
Abstract: *The highest chemoselective synthesis of 4-vinylcyclohexene ever observed by butadiene cyclodimerization on nickel complexes has been obtained with aminophosphinephosphinite and bis(aminophosphine) chiral ligands (selectivity up to 99%).*

Butadiene cyclodimerization has been extensively studied by Wilke's group since the early sixties.[1] The association of zerovalent nickel with phosphorus ligands in an aprotic solvent gives rise to the production of a mixture of 4-vinylcyclohexene (VCH), cycloocta-1,5-diene (COD) and *cis*-1,2-divinylcyclobutane (DVCB) as shown in Scheme 1.



Scheme 1

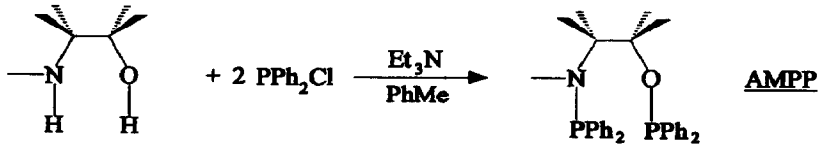
According to the ligand structure, COD has been obtained selectively with sterically hindered phosphites.[2] As within these compounds 4-vinylcyclohexene is the only butadiene asymmetric cyclodimer, it is so of great interest to try to develop new ligands which could enhance both the chemo and the enantioselectivity, thus providing a useful way to the production of a chiral synthon by catalytic C-C bond formation from this very cheap starting material.

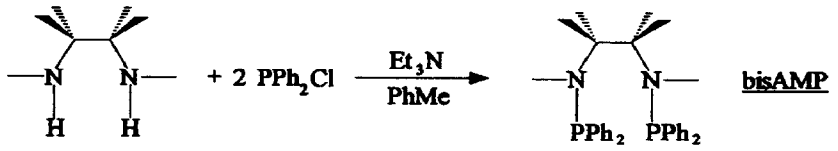
So far, the asymmetric synthesis of 4-vinylcyclohexene on nickel catalysts has been the subject of few studies, where low selectivities and moderate optical yields (up to 26%[5]) have been obtained, in the presence of dioxaphospholane ligands,[4] as well as oxazaphospholanes and aminophosphinephosphinites ligands (AMPP),[5] the latter beeing used in a ligand / nickel ratio of 1.

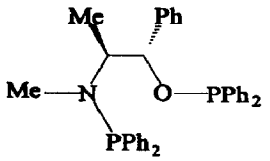
We wish now to report that upon using a ligand / nickel ratio of 2 either with AMPP ligands ((1*S*,2*S*)-Ψ-Ephos 1, (1*R*,2*S*)-Ephos 2 and (*S*)-ProNOP 3) or with bis(aminophosphine) (bisAMP) ligands ((*S*)-ProNNP 4

and N,N'-(diphenylphosphino)-N,N'-(dimethyl)ethylenediamine 5), an exceptional enhancement of chemo--selectivity is observed.

These ligands were prepared according to procedures already described , [6] by diphosphinylation of (1*S*,2*S*)-Ψ-Ephedrine, (1*R*,2*S*)-Ephedrine, (*S*)-Prolinol, (*S*)-2-(anilinomethyl)pyrrolidine and N,N'-(dimethyl) ethylenediamine, to give respectively the (1*S*,2*S*)-Ψ-Ephos, (1*R*,2*S*)-Ephos, (*S*)-ProNOP, (*S*)-ProNNP and the N,N'-(diphenylphosphino)-N,N'-(dimethyl)ethylenediamine ligands as shown in Scheme 2.

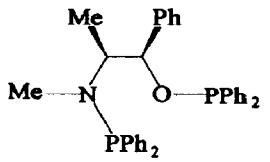






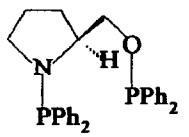
1

(1*S*, 2*S*)-Ψ-Ephos



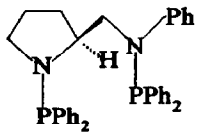
2

(1*R*, 2*S*)-Ephos



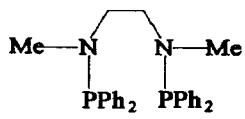
3

(*S*)-ProNOP



4

(*S*)-ProNNP



5

N,N'-(diphenylphosphino)-
N,N'-(dimethyl)ethylenediamine

Scheme 2

In a typical butadiene dimerization experiment, the reaction was conducted under nitrogen upon using 27.5 mg (0.1 mmol) of bis(cycloocta-1,5-diene)nickel and 1 or 2 equivalents of the corresponding ligand dissolved in 8 ml of dry and degassed toluene in a glass reactor closed with a teflon stopper. Butadiene (0.43 g,

8 mmol) was added as a liquid in this reactor which was heated at the desired temperature. The solution was stirred and samples of the reaction mixture were taken from time to time after freezing and analysed by G.L.C. for conversion and selectivities by using *n*-heptane as internal standard.

Typical results are reported in the table, and compared to other results obtained in the literature.

Table : 4-Vinylcyclohexene Synthesis on Phosphane-Nickel Catalysts [a].

Entry	Ligand	Ligand / Nickel	Temp. [°C]	Time [h]	Conv. [%]	Yield [%] VCH	Yield [%] COD	E.e.[c] [%]	Config.	Ref.
1 [b]	PPh_3	2	60	15	100	37	63	-	-	3
2 [b]	PPh_3	100	60	15	100	60	40	-	-	3
3	Ph_2PNMe_2	2	60	2	100	29	71	-	-	-
4	Dppb [d]	1	70	96	100	5 [e]	34 [e]	-	-	-
5	Dppb [d]	2	70	96	100	15 [e]	42 [e]	-	-	-
6	Diop [f]	1	-	-	-	17	83	< 3	nd	4
7	1	1	40	19	90	41	59	21	*S*	5
8	1	2	60	72	4	99	1	nd	nd	-
9	1	2	80	70	100	99	1	< 3	*R*	-
10	2	1	40	19	90	40	60	< 3	*S*	5
11	2	2	80	72	50	99	1	< 3	*R*	-
12	3	1	40	24	90	62	38	7	*S*	-
13	3	2	70	66	26	94	6	nd	nd	-
14	4	1	60	24	90	90	10	10	*S*	-
15	4	1	80	17	100	80	20	6	*S*	-
16	4	2	70	24	90	98	2	10	*S*	-
17	5	1	60	24	38	78	22	-	-	-

[a] Experimental conditions : see text.

[b] Butadiene / nickel = 170; $[Ni]_O$= 40 mmol/l; Solvent = anhydrous toluene

[c] Determined on the basis of the optical rotation for the optical pure (*S*)-enantiomer of VCH · $[\alpha]_D^{25}$ = + 109 (c = 4.1, toluene).[7]

[d] Dppb = 1,4-bis(diphenylphosphino)butane.

[e] With the Dppb ligand, the major product is the cyclododeca-1,5,9-triene trimer which is respectively formed with a selectivity of 61% and 43% according to the 1 or 2 ligand / nickel ratio.

[f] Diop = [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphine).

The analysis of the results leads to the following comments :

(i) Whatever the ligand, the optical yield remains lower than the best one reported in the literature (26%[5]).

(ii) Monodentate phosphine and aminophosphine ligands seem to be less suitable for a selective synthesis of VCH than the bidentate ones. Indeed, with triphenylphosphine as ligand, Heimbach noted a VCH selectivity enhancement only up to 60% even upon increasing the PPh_3 / Ni ratio to 100 (Entries 1, 2).[3] In the same way, while a VCH / COD ratio of 4 is obtained with the ligand 5-nickel catalyst, this ratio drops to 0.4 when the corresponding monodentate system is used (in these two cases, P / Ni = 2) (Entries 17, 3).

(iii) Among the bidentate ligands of the table (and for a ligand / nickel ratio of 1), it appears than our AMPP and bisAMP ligands are the most selective ones into VCH (Entries 7-17). Indeed, for the Diop and Dppb ligands, in which the diphenylphosphino groups are bound to a carbon atom and not to a nitrogen or an oxygen atom, the major product is respectively cycloocta-1,5-diene and the cyclododeca-1,5,9-triene trimer (Entries 4-6).

(iv) The main feature observed in this series of experiments is that, upon increasing the ligand / nickel ratio from 1 to 2, a selectivity into VCH up to 99% is reached by using AMPP and bisAMP ligands. Nevertheless, in the case of the AMPP, the excess of ligand reduces the activity (Entries 7-13) to such an extent that it is necessary to increase the reaction temperature in order to obtain good conversions (Entries 8, 9). In addition, for the (1*S*,2*S*)-Ψ-Ephos, a decrease of enantioselectivity and even the opposite enantiomer is observed though in very low e.e.. Either a temperature effect or the occurence of different catalytic bidentate or monodentate species could explain this behaviour (Entries 7, 9).

(v) It is also noteworthy that upon using the (*S*)-ProNNP ligand, only one equivalent of this bis(amino--phosphine) compound is required to induce similarly a high chemoselectivity into VCH (Entry 14). Again, upon using 2 equivalents of (*S*)-ProNNP, this selectivity is enhanced to 98% but in this case with no loss of enantioselectivity and activity (Entries 14, 16).

This particular behaviour of the (*S*)-ProNNP, as compared with the AMPP ligands, is beeing examined in other asymmetric catalytic reactions we are currently studying in our laboratory.[8]

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