were made possible by a NATO Research Grants Programme. The work was carried out with the financial support of the Ministry of Public Education, Rome.

Registry No. **1**, 34160-17-3; **2**, 110972-21-9; **3**, 110972-22-0; **4**, 110972-23-1; *N*-phenyl-1-naphthylamine, 90-30-2; *N*-(3-ethylphenyl)-1-naphthylamine, 95275-66-4; 1-naphthylamine, 134-32-7; 3-ethylaniline, 587-02-0.

Nickel-Catalyzed Codimerization of 1,3-Cyclohexadiene and Vinyltrimethylsilane. Effects of Organophosphorus Ligands

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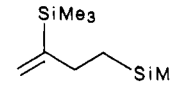
Recent progress achieved by using organosilicon compounds has offered several new aspects to synthetic organic chemistry.[1] One of them is the use of vinylsilane as a masked carbonyl functionality[2] and as a possibility for generation of α-silyl carbanions through the addition of different types of carbanionic species on the activated double bond.[3] Another interesting feature in respect to synthesis results from the electrophilic substitution reactions.[4] Recently, we reported a high enantioselectivity (93% ee) in the asymmetric hydrovinylation of 1,3-cyclohexadiene catalyzed by the Ni(COD)$_2$–AlEt$_2$Cl–(2*R*,3*R*)-threophos system.[5] The catalytic cyclodimerization of 1,3-dienes with miscellaneous olefins is an attractive route to interesting synthons. Unfortunately, this reaction fails in more general cases.[6,7] Miller et al.[8] was the first to report the codimerization of ethylene and 1,3-cyclohexadiene catalyzed by nickel complexes and we describe herein that Ni(COD)$_2$–AlEt$_2$Cl–L (in 1/6/2 molar ratio) modified with suitable organophosphorus P(III) ligands L is able to catalyze a codimerization reaction between 1,3-cyclohexadiene (**1**) and vinyltrimethylsilane (VTMS **2**) (**1**/**2**/Ni = 50/50/1) in toluene solution at 50 °C. As shown in Table I and Scheme I, after 48 h of reaction, the expected compound 3-[1-(trimethylsilyl)vinyl]cyclohexene (**3**) and the oligomer byproducts 2,4-bis(trimethylsilyl)-1-butene (**4**) and (*E*)- and (*Z*)-1,4-bis(trimethylsilyl)-3-butene (**5**, **6**) were formed. The latter compounds have been already obtained by the oligomerization of VTMS catalyzed by the catalytic system prepared from AlEt$_3$ reduction of nickel acetylacetonate Ni(acac)$_2$ in the presence of triphenylphosphine with dichloroethylene as solvent;[9]



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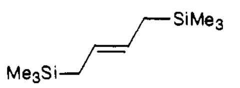

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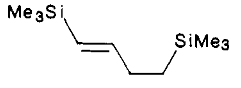
these products probably result from isomerization of (*Z*)- and (*E*)-1,4-bis(trimethylsilyl)-1-butenes (**7**, **8**), previously prepared in the VTMS dimerization by using NiCl$_2$–Al$_2$Et$_3$Cl$_3$–PPh$_3$ as the catalytic system.[9] Under our catalytic conditions the compounds **5** and **6** are the minor products. The major byproduct resulting from homoligomerization of VTMS is compound **4**. Unlike the Ni(0)-catalyzed cooligomerization of VTMS with 1,3-dienes such as butadiene[10,11] and isoprene,[12] the compounds **3** and **4** result from the C–C bond formation between the α-carbon of VTMS and either 1,3-cyclohexadiene or VTMS, whatever the nature of the ligand (see Table I). Such an addition was observed in accordance with our results in the cooligomerization of butadiene–VTMS over a nickel chloride catalytic system in the presence of an organoaluminum Lewis acid and triphenylphosphine.[13] Indeed, we never observed the inverse addition with the formation of 3-[2-(trimethylsilyl)vinyl]cyclohexene (**9**).



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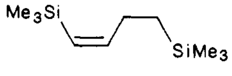

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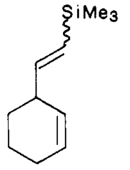

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It can be seen from Table I that the nature of the phosphorus ligand and the P/Ni ratio strongly affect both catalytic activity and product selectivity. The ligand is essential for the formation of **3** (run 5) as is the organoaluminum Lewis acid, without which the reaction fails to give any of the desired products. The best results are obtained with triethyl phosphite (run 10) and bis(dimethylamino)phenylphosphine (run 13) as ligands and with a P/Ni ratio of 2/1 and AlEt$_2$Cl/Ni(COD)$_2$ ratio of 6/1 at 50 °C.[16] The chelating 1,2-bis(diphenylphosphino)ethane inhibits the catalyst activity for L/Ni = 2 and 1 and becomes only active with a L/Ni = 0.5. Such an effect has already been observed with chelating

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[16] With either a higher temperature or a higher ratio of AlEt$_2$Cl/Ni the selectivity decreases for **3** and increases for **5** and **6**. For instance other things being equal, with PPh$_3$ as ligand at 110 °C, **3**/**4**/**5**/**6** were obtained in 11/31/46/12% selectivity and for an AlEt$_2$Cl/Ni ratio of 8 at 50 °C the selectivity was 36/56/6/2; both experiments gave the same VTMS conversion (60%) in 40% chemical yield.

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Table I. Codimerization of 1,3-Cyclohexadiene and VTMS[a]

runs	ligands	θ,[b] deg	L/Ni	VTMS conversn, %	chemical yield,[c] %	product selectivity, % 3	4	5	6
1	PPh_3	145	4	9	9	96	4	0	0
2	PPh_3		3	26	20	64	23	8	5
3	PPh_3		2	44	30	45	37	11	7
4	PPh_3		1	55	37	36	59	3	2
5			0	2	1	0	100	0	0
6	$P(Ph\text{-}o\text{-}OMe)_3$	190–200	2	13	10	58	31	6	5
7	$PPh_2(CH_2)_2PPh_2$	125	0.5	65	40	20	78	1	1
8	Ph_2POEt	133	2	36	27	59	39	1	1
9	$PhP(OMe)_2$	115	2	62	47	58	39	2	1
10	$P(OEt)_3$	109	2	80	56	46	54	0	0
11	$P(OPh)_3$	128	2	50	32	30	64	3	3
12	$Ph_2P(NMe_2)$	149	2	76	50	36	56	5	3
13	$PhP(NMe_2)_2$	153	2	79	54	43	53	2	2
14	$P(NMe_2)_3$	157	2	61	43	51	47	1	1
15	$Ph_2PN(i\text{-}Pr_2)$	155–160	2	63	38	17	78	3	2

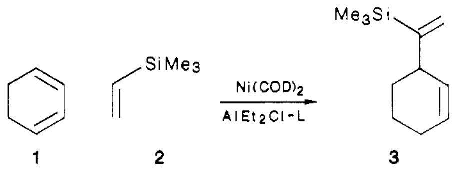
[a] Reaction conditions: temperature, 50 °C; reaction time, 48 h; $AlEtCl/Ni(COD)_2 = 6/1$; VTMS/1,3-cyclohexadiene/Ni = 50/50/1; $[Ni(COD)_2] = 0.140$ mol/L; solvent, toluene. [b] Tolman parameters.[14,15] [c] For each run the chemical yield was calculated from the ratio of the amount of the reaction products and the amount of the starting compounds.

Table II. Influence of the Catalytic Precursors on the Codimerization of 1,3-Cyclohexadiene and VTMS[a]

reducing agent Ni	Al	Al/Ni	reactn time, h	VTMS conversn, %	chemical yield, %	product selectivity, % 3	4	5	6
$NiCl_2$	$AlEt_2Cl$[b]	7.8	19	6	6	92	8	0	0
$NiCl_2$	$AlEt_2Cl$	8	26	10	10	96	4	0	0
$NiCl_2$	$AlEt_2Cl$	8	49	17	15	85	10	3	2
$NiCl_2$	$AlEt_2Cl$	8	65	72	46	29	28	34	9
$Ni(acac)_2$	$AlEt_2Cl$	6	48	47	30	29	46	18	7
$Ni(acac)_2$	$AlEt_2Cl$[c]	6	48	63	35	18	25	45	12

[a] Reaction conditions: L = PPh_3; L/Ni = 2; Ni = 0.14 mol/L; temperature, 50 °C; VTMS/1,3-cyclohexadiene/NiX_2 = 50/50/1. [b] $AlEt_2Cl$ (2 equiv) was added to $NiCl_2 + PPh_3$, and then the complement (5.8 equiv) was added after the addition of VTMS and 1,3-cyclohexadiene. [c] $Ni(acac)_2$ was reduced by $AlEt_3$ (1 equiv) in the presence of PPh_3, and $AlEt_2Cl$ (6 equiv) was added.

Scheme I. VTMS and 1,3-Cyclohexadiene Codimerization



bisphosphines in the butadiene–ethylene codimerization[17] and in the propylene dimerization.[18,19] From these results our primary premise is that the VTMS conversion and the chemical yields depend probably on the size of the ligands. The chemical yields are at a minimum for ligands for which the steric parameter θ is between 130 and 140° and lie at a maximum for values of θ either above 140° or below 130° except for ligand $P(Ph\text{-}o\text{-}OMe)_3$, which probably has a chelating effect because of the *o*-methoxyl group. On the other hand, it is more difficult to draw definitive conclusions about electronic effects proportional to $\lambda\text{co}(A_1)$ of $R_3P\text{–}Ni(CO)_3$ for the selected ligands from these results. In order to increase the chemical yield and the selectivity for **3**, we have tested different catalytic precursors.

As shown in Table II for ligand PPh_3, and by using identical reaction conditions, after a 48-h reaction time the selectivity is greatly modified in favor of homoligomerization products. These catalytic systems do not lead to any significant improvements in these reactions. With the different catalytic systems studied, the selectivity for **3** is highest at low VTMS conversion. We have not yet found a reason for the selectivity variation of **3** vs reaction time. The mechanism of catalytic oligomerization of ethylene–diene has been the subject of several proposals. In general, two different mechanisms are discussed: a hydride mechanism[6,8,21] and a mechanism based on cyclic intermediates.[6,20] However, the catalytic systems used, obtained by treating either $Ni(COD)_2$ or NiX_2L_2 (X = anionic ligand) with an aluminum alkyl, are believed to involve Ni(H)(Y)L, where Y is a complex Lewis acid anion of the type AlR_xX_{4-x}.

In conclusion, the work described in this paper reveals for the first time a codimerization reaction between a cyclic diene and vinyltrimethylsilane, and although the chemical yields are modest, the obtained compound **3** is an ideal synthon for the entry to methylene lactone synthesis according to Yu and Helquist's synthetic approach,[22] if we consider the vinyl trimethylsilyl group as a synthetic equivalent of the acrylic acid group.[23]

Experimental Section

General Procedures. All reactions of organometallic reagents and other air-sensitive materials were performed under nitrogen. Solutions of these materials were transferred with hypodermic needles. Toluene was distilled from sodium. All commercial chemicals and reagents were distilled or recrystallized prior to use. Triethylamine was stored over activated 3-Å molecular sieves.

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The different ligands Ph_2POEt, $PhP(OMe)_2$, Ph_2PNMe_2, $PhP(NMe_2)_2$, and $P(NMe_2)_3$ were prepared according to classic methods.[24] The synthesis of ligand $Ph_2PN(i\text{-}Pr)_2$ is described below. Crude products were generally prepurified by Kugelrohr distillations on a Büchi GKR-50 apparatus. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded respectively at 100, 25.144, 40, and 48 MHz on a Bruker AC 100 spectrometer. The NMR spectra were obtained from $CDCl_3$ solutions unless otherwise stated. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C and 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative; the coupling constants are given in hertz. Multiplicities are expressed as follows: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. In ^{13}C NMR spectra, basic DEPT sequence[25] was used to determine the structure of compounds **3**–**6**. The ^1H NMR peak areas are expressed as the number of hydrogen atoms (H). The IR spectra were obtained on a Perkin-Elmer Model 298 from neat liquid films. The analytical results agree with calculated values within 0.3%. Analytical gas–liquid chromatography (GLC) was performed on an Intersmat IGC 121 FL instrument with a flame-ionization detector and helium carrier gas (1.0–1.3 kg/cm^2) using a CP Sil 5 fused silica 20-m capillary column. Codimerization reactions were monitored on CPG capillary column by using undecane as internal standard. Calibration curves can be prepared by plotting peak areas against corresponding concentrations. CPG conditions: $P(H_2)$ and carrier gas, helium 1 bar; injector and detector temperature, 220 °C; isotherm for 3 min, linear temperature programmed from 35 to 120 °C by 7 °C/min; the different retention times in minutes are 10.76 (**3**), 8.45 (**4**), **5** 9.10 (**5**), 9.18 (**6**), and 9.55 (undecane).

(*N,N*-Diisopropylamino)diphenylphosphine. To a solution of *N,N*-diisopropylamine (5.05 g, 0.05 mol) and triethylamine (0.05 mol) in benzene (50 mL) was added dropwise a solution of chlorodiphenylphosphine (11.03 g, 0.05 mol) and benzene (20 mL) at room temperature under N_2 atmosphere. The resulting mixture was stirred and heated with reflux for 4 h and allowed to cool to room temperature. The triethylammonium chlorohydrate was collected on a glass filter and washed with diethyl ether. The combined organic phases were concentrated under vacuum to afford a viscous yellow oil, which crystallized from petroleum ether/diethyl ether in 1/1 ratio and in 89% chemical yield to give the product: mp 76–80 °C; ^1H NMR (C_6D_6) δ 1–1.40 (d, 6 H), 3.2–3.7 (m, 1 H), 7.1–7.6 (m, 10 H); ^{13}C NMR (C_6D_6) δ 24 (d, $^3J_{CP}$ = 6.3 Hz, CH_3), 47.8 (d, $^2J_{CP}$ = 8.4 Hz, CH), 128.2–133.4 (m, Ph); ^{31}P NMR (C_6D_6) δ 38. Anal. Calcd for $C_{18}H_{24}NP$: C, 75.79; H, 8.42; N, 4.91. Found: C, 75.95; H, 8.36; N, 4.69.

TMVS and 1,3-Cyclohexadiene Codimerization. The catalyst $Ni(COD)_2$ (2 mmol) and organophosphorus ligand (2 mmol) were dissolved in 2 mL of toluene under a N_2 atmosphere at room temperature. The solution was stirred for 10 min and then transferred into a glass reactor containing 1,3-cyclohexadiene (0.1 mol) and VTMS (0.1 mol). To the stirred mixture was added a (1 M) solution of $AlEt_2Cl$ (12 mmol) in toluene (12 mL). It is important that this sequence of events be adhered to strictly, otherwise the reaction fails to give any product. The mixture was stirred for 48 h at 50 °C. Workup consisted of the addition of H_2O (10 mL) to the reaction mixture. Then the reaction products were extracted with diethyl ether (5 × 20 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum, and the reaction products were distilled under vacuum on a spinning band column. *n*-Undecane was added to the products to follow the codimerization reaction, and the mixture was analyzed on GLC.

2,4-Bis(trimethylsilyl)-1-butene (4): bp 38 °C (2 mm), $n^{20}{}_D$ 1.4381 [lit.[13] bp 70.71 °C (25 mm), $n^{20}{}_D$ 1.4382]; IR, strongest bands 1480, 1250, 920, 850–870, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.13 (s, 9 H), 0.48–0.78 (m, 2 H), 1.93–2.32 (m, 2 H), 5.18–5.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.71 ($Si(CH_3)_3$), −1.33 ($Si(CH_3)_3$), 15.9 (CH_2), 29.82 (CH_2), 154.9 (C) 122.25 (CH). Anal. Calcd for $C_{10}H_{24}Si_2$: C, 59.94; H, 11.98. Found: C, 59.69; H, 11.60.

(*Z*)- and (*E*)-1,4-Bis(trimethylsilyl)-2-butenes (5, 6): bp 46 °C (2 mm), $n^{20}{}_D$ 1.4416, cis/trans ratio 1/2 [lit.[13] 90–91 °C (28 mm), $n^{20}{}_D$ 1.4412, cis/trans ratio 1/1]; IR, 3020, 1610, 1260, 1150, 1050, 810–870, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.02 (s, 9 H), 0.04 (s, 9 H), 1.49–1.55 (m, 4 H), 5.15–5.20 (m, 2 H); ^{13}C NMR (trans isomer **5**) δ −1.93 (s, $Si(CH_3)_3$), 22.83 (CH_2), 124.33 (CH); (cis isomer **6**) δ −1.70 (s, $Si(CH_3)_3$), 17.81 (CH_2), 123.12 (CH). Anal. Calcd for $C_{10}H_{24}Si_2$: C, 59.94; H, 11.98. Found: C, 59.71; H, 11.70.

3-[1-(Trimethylsilyl)vinyl]-1-cyclohexene (3): bp 30–35 °C (0.5 mm), $n^{21}{}_D$ 1.4802; IR, 3020, 1450, 1410, 1250, 840, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 9 H), 1.1–2.1 (m, 6 H), 2.80–3.04 (m, 1 H), 5.31–5.85 (m, 4 H); ^{13}C NMR ($CDCl_3$) −0.85 ($SiMe_3$), 20.75 (CH_2), 25.06 (CH_2), 29.91 (CH_2), 40.98 (CH), 124.84 (CH), 127.44 (CH), 130.77 (CH_2), 156.02 (C). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.29; H, 11.10. Found: C, 73.13; H, 11.05.

Registry No. **1**, 592-57-4; **2**, 754-05-2; **3**, 110434-24-7; **4**, 53304-31-7; **5**, 16054-35-6; **6**, 16054-34-5; $Ph_2PN(i\text{-}Pr)_2$, 22859-57-0; $HN(i\text{-}Pr)_2$, 108-18-9; Ph_2PCl, 1079-66-9; $Ni(COD)_2$, 1295-35-8; $AlEt_2Cl$, 96-10-6; PPh_3, 603-35-0; $P(Ph\text{-}o\text{-}OMe)_3$, 4731-65-1; $PPh_2(CH_2)_2PPh_2$, 50819-15-3; $PhP(OMe)_2$, 2946-61-4; $P(OEt)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; $Ph_2P(NMe_2)$, 6840-01-3; $PhP(NMe_2)_2$, 6143-71-1; $P(NMe_2)_3$, 1608-26-0; Ph_2POEt, 719-80-2; $NiCl_2$, 7718-54-9; $Ni(acac)_2$, 3264-82-2.

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Selective Hydroboration Studies with Acetoxyborohydride

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The remarkable facile monohydroboration of dienes, alkynes, or enynes has opened a new and convenient route to large number of unsaturated organoboranes. It is now possible with the choice of a suitable hydroborating reagent to selectively hydroborate either a mono- or disubstituted terminal double bond[1] of the diene or an internal carbon–carbon triple bond[2] or terminal double bond[3] of an enyne, and the diene containing terminal and internal carbon–carbon double bonds preferentially undergoes hydroboration at the terminal position.[4] This unique selectivity in hydroboration and the options for further manipulation of the intermediate organoboranes to a variety of organic molecules have recently been reviewed by us.[5] The lack of any general procedure for the hydroboration of an internal carbon–carbon double bond of a diene in the presence of terminal one prompted us to employ acetoxyborohydride ($CH_3COOB^-H_3$) as the hydroborating agent. It has been reported[6] that the reagent can tolerate some functional groups, is sluggish in hydroboration, and is convenient to prepare.

The acetoxyborohydride, as a hydroborating reagent, has a special significance for the synthesis of alkyl iodide via iodination since it gives mainly "RBH_2" and some "R_2BH" species.[6] The trialkylborane (R_3B) obtained from diborane has obvious disadvantage in iodination as only two alkyl groups are utilized in the formation of alkyl iodide.[7-10]

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