Table I. Enantioselective Protonation of Enolates **2** of Schiff Base Methyl Esters **1** by Diacyltartaric Acids **3**

racemic Schiff base	acid	active Schiff base		
		obsd $[\alpha]^{25}$D,[a] deg, in CHCl₃ (c)	enantiomeric ratio S:R	chemical yield,[e] %
1a	**3a**	−41.9 (3.3)	79:21[b,c]	85
	3b	−13.6 (3.4)	59:41	84
	3c	−28.2 (3.3)	70:30	82
	3d	−10.3 (3)	57:43	80
	3e	−6.95 (2.4)	55:45	81
	3f	−5.36 (3)	54:46	83
	3g	−28.96 (3,3)	70:30	85
	3h	−30.1 (2)	71:29	85
	3i	−21.1 (3.3)	65:35	86
	3j	−44.7 (1.5)	81:19	79
1b	**3a**	−66.15 (2.4)	63:37	65
	3b	−19.6 (3.1)	54:46	64
	3c	−43.36 (4)	59:41	65
	3d	−82.06 (4)	67:33	60
	3e	−36.75 (3.3)	57:43	61
	3f	−7.35 (2.5)	51:49	64
1c[d]	**3a**	−88.45 (2.5)	65:35	95
	3b	−31.03 (2)	55:45	93
	3c	−42.34 (2.4)	57:43	92
	3d	−36.54 (2.8)	56:44	90
	3e	−11 (2.2)	52:48	95
	3f	−20.3 (2)	53:47	95
1d	**3a**	−43.55 (4.5)	67:33[c]	82
	3d	−50.05 (2.6)	69:31[c]	76
	3h	−45.5 (4.5)	67:33	80

[a] References (CHCl₃) (this work): **1a**, R, $[\alpha]^{25}$D +71.5° (c 3); **1b**, S, $[\alpha]^{25}$D −245° (c 4) **1c**, S, $[\alpha]^{25}$D −290° (c 3); **1d**, S, $[\alpha]^{25}$D −130° (c 4). All rotations were measured in a 1-mL cell (10 cm) on a Perkin-Elmer Model 241 polarimeter. [b] This corresponds to an enantiomeric excess (% ee) of 58%. [c] These results were confirmed by NMR analysis in the presence of tris(3-heptafluoropropylhydroxymethylene)-D-camphoratoeuropium. The signals followed were PhC*H* for **1a** and COOCH₃ for **1d**. The corresponding racemic products gave two equal signals in the same conditions, while the optically pure products gave a single one. [d] One equivalent of N-benzylidenetryptophan methyl ester is treated by 2.5 equiv of LDA, and then by 3.5 equiv of diacyltartaric acid. [e] The chemical yields correspond to recrystallized product for **1a**, **1b**, and **1c**, and to crude product for **1d**.

after acidification (95% yield, $[\alpha]^{25}$D −24.1° (c 2, dioxane)).

Our results show that the enantiomeric ratios of Schiff base esters **1** are largely affected by the structure of the acid **3** used for the protonation. The asymmetry of the reaction seems to be favored by the proximity of the hindering group contained in R² and the carboxyl group. On the other hand, enantiomeric enrichment does not decrease gradually when the distance between the hindering group and the carboxyl group increases.

The present method is simple and versatile. It has the advantages of giving Schiff base esters **1** in good enantiomeric purity in the best cases from their racemic mixture in a one-pot reaction, which would allow easy preparation of optically active α-amino acids, as well as easy recovery of the chiral reagent **3** for reuse without any racemization. Further studies are in progress.

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*Received July 17, 1978*

Metallacyclopentanes as Catalysts for the Linear and Cyclodimerization of Olefins

Sir:

Transition metals can catalyze the dimerization of olefins to either cyclo-[1] or linear[2] dimers. Linear dimers are produced by a large number of catalytic systems while only very specific catalysts have been observed to cyclodimerize strained olefins.[3] Cyclodimers have not been observed from simple, unstrained unsaturated hydrocarbons. In most cases, the linear dimers are the result of metal hydride catalysts,[2,4,5] while cyclodimerization appears to proceed through metallacyclopentane intermediates.[6]

We recently reported that phosphine nickelacyclopentanes decomposed to produce cyclobutane, ethylene, or 1-butene depending on the coordination number of the complex[7] and that a bisethylene complex was in equilibrium with the metallacycle.[8]
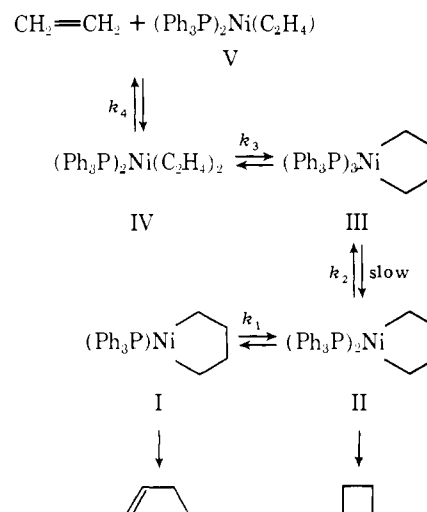
These observations suggested that the nickelacyclopentane III might be a catalyst for the formation of dimers from ethylene.

Consequently, when tris(triphenylphosphene)tetramethylenenickel(II) (III) was dissolved in toluene and treated with ethylene (80 psi), cyclobutane[9] and butenes were formed. As can be seen in Table I, the products were produced catalytically. Since the production of the proposed reaction interme-

Table I. Catalytic Dimerization of Ethylene at 80 psi by Tris(triphenylphosphine)tetramethylenenickel(II)

(Ph₃P)₃Ni, M	solvent[a]	temp, °C	time, h	turnover,[b] C₄/Ni	products	
					% cyclobutane	% butenes
0.0023	T	0	72	13	72	28
0.011	T	23	21	9	54.5	45.5
0.01	T	45	20	17.6	43.2	56.8
0.0091	T	80	19	22.7	8.4	91.6
0.002	T + 15% LiCl	0	72	6.7	10.8	89.2
0.002	chlorobenzene	0	14	59.5	0.06	99.4

[a] T = toluene. [b] C_2H_4/catalyst = 250–280 (80–90 psi at 25 °C).

diates required a number of phosphine equilibration steps, the observed changes in selectivity and activity with variations in the catalyst concentration, temperature, and solvents were reasonable. Passive solvents such as toluene resulted in the production of cyclobutane while chlorobenzene produced a very active catalyst for the linear dimerization of ethylene to 1-butene. This reaction probably did not involve a metallacyclic
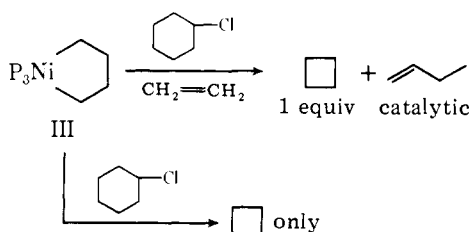

intermediate since the nickelacycle on decomposition in chlorobenzene produced cyclobutane as the major stoichiometric product.

However, this catalyst system did not require an aluminum alkyl cocatalyst as do the more standard nickel oligiomerization catalysts.[10]

In order for the reaction to be catalytic in nickel, ethylene complexes of nickel[11] must revert to metallacycles under ethylene pressure. Consequently nickel–phosphine complexes of ethylene were examined. It was found that the reaction of
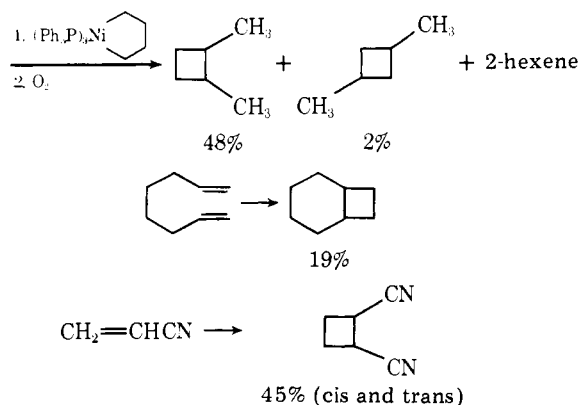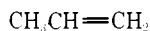
$(Ph_3P)_2Ni(C_2H_4) + C_2H_4$
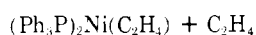
V
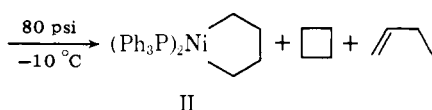
bis(triphenylphosphine)ethylenenickel(0) (V) (−10 °C, 72 h) with 80 psi of ethylene produced a 25% isolated yield of the metallacycle II.

Cyclobutane (20%) and 1-butene were also produced in this reaction. A more active catalyst could be prepared by the addition of 1 equiv of phosphine to the solution of V. Primary

$CH_3CH=CH_2$

olefins were not catalytically cyclodimerized. Propylene, 1,7-octadiene, and acrylonitrile reacted with the parent metallacycle to produce new substituted metallacycles as well as linear dimers. The substituted metallacycles could be converted to cyclobutane derivatives by oxidative decomposition.[12,13]

For example, 1,2-dicyanocyclobutane was prepared by allowing a solution of 0.72 g (0.8 mM) of III and 3 mL of acrylonitrile to warm from −20 °C to room temperature over a 48-h period. The flask was then cooled to −78 °C, evacuated, and filled with O_2. After connection to a bubbler, the flask was warmed slowly to room temperature. The product was purified by GLC and compared spectroscopically with an authentic sample of *cis*- and *trans*-1,2-dicyanocyclobutane.[14]

This work demonstrates that metallacycles can play a major role in the dimerization of olefins to produce products normally not obtained by usual metal hydride catalysts, and represents the first example of the catalytic production of cyclobutane from ethylene.

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(9) Cyclobutane produced in this reaction was purified by GLC (Duropak, 15 ft, 65 °C) and showed a single peak at δ 1.96 (CDCl₃ solvent) in the ¹H NMR spectrum and showed a typical cracking pattern in the mass spectrum, *m/e* 56 (62.1, M⁺), 42 (2.9, C₃H₆⁺), 28 (100, C₂H₄⁺), identical with standard sample prepared by the method reported by T. Kametani and Y. Nomura, *J. Pharm. Soc. Jpn., Engl. Transl.*, **74**, 1037 (1954).
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(12) Reaction products were purified by GLC (Carbowax, 32 ft, 75 °C) and identified as 1,2-dimethylcyclobutane and 1,3-dimethylcyclobutane, respectively, on a basis of their different mass spectral cracking pattern and their NMR spectra. The characteristic difference is in the intensity of the peaks produced by the cycloreversion reaction. The 1,2 isomer produced both ethylene and propylene while the 1,3 isomer produced minimal amounts of ethylene. Dimethylcyclobutane: *m/e* 84 (3.9, M⁺), 69 (4.4, C₅H₉⁺), 56 (60.9, C₄H₈⁺), 42 (100, (C₃H₆⁺), 28 (84.4, C₂H₄⁺). 1,3-Dimethylcyclobutane: *m/e* 84 (4.1, M⁺), 69 (6.3, C₅H₉⁺), 56 (53.7, C₄H₈⁺), 42 (100, C₃H₆⁺), 28 (20.1, C₂H₄⁺). These are nearly identical with the reported values. L. Dor. J. Momigny, and P. Natails, *Adv. Mass Spectrom.*, **2**, 370 (1961), and K. Griesbaum and P. E. Butler, *Angew. Chem., Int. Ed. Engl.*, **6**, 4444 (1967). The ¹H NMR spectrum of 1,2-dimethylcyclobutane showed peaks at δ 0.91 (unresolved d, 6 H), 1.62 (m, 2 H, 1.97 (br s, 4 H). The spectra suggested that a mixture of cis and trans isomers was produced in this reaction.
(13) Bicyclo[4.2.0]octane: ¹H NMR (in CDCl₃) δ 1.50 (m, 8 H), 1.83 (m, 4 H); mass spectrum (16 eV) *m/e* 110 (C₈H₁₄); bp 130–132 °C (760 mmHg). The isolated *trans*-2-nickelahydrindan complex, which was the intermediate

of this reaction, produced bicyclo[4,2.0]octane by oxidative decomposition (bp 129–131 °C (760 mmHg)) which appeared to be the trans isomer, while the cis-2-nickelahydrindan complex afforded the cis isomer (bp 136–139 °C (760 mmHg)); cf. bp 136–138 °C (760 mmHg) of A. T. Blomquist and J. Kwiatek, *J. Am. Chem. Soc.*, **73**, 2098 (1951). Details are given in ref 6b.

(14) The product was compared with an authentic sample of cis- and trans-1,2-dicyanocyclobutane obtained from Aldrich Chemical Co.: NMR δ 3.45 (m, 2 H), 2.40 ppm (broadened d of d, 4 H). The GLC trace was similar to that of the commercial isomer mixture.

(15) A. Miyashita and R. H. Grubbs, unpublished results.

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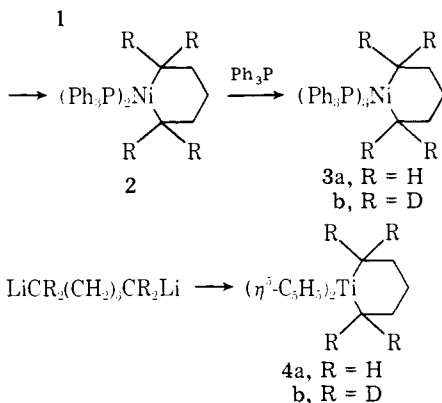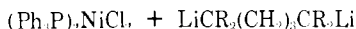**Robert H. Grubbs,*[16] Akira Miyashita[16]**
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## Carbon–Carbon Bond Cleavage Reactions in the Decomposition of Metallacycles

Sir:

We recently reported that trisphosphine and five-coordinate nickelacyclopentanes and titanacyclopentanes decomposed by β-C–C bond cleavage to produce ethylene. To determine if C–C bond cleavage would occur in systems which could not produce stable metal–olefin complexes, metallacyclohexanes were prepared. Bis(triphenylphosphine)dichloronickel(II) and titanocene dichloride were treated with 1,5-dilithiopentane (**1**) at low temperature to yield **2** and **4** which were purified and analyzed by procedures similar to those used in the preparation of the related metallacyclopentanes.[1a,2,3]

$(Ph_3P)_2NiCl_2 + LiCR_2(CH_2)_3CR_2Li$

2   3a, R = H
      b, R = D

4a, R = H
b, R = D

$(\eta^5\text{-}C_5H_5)_2TiCl_2 + LiCR_2(CH_2)_3CR_2Li \longrightarrow (\eta^5\text{-}C_5H_5)_2Ti$

The yields of the decomposition products of **2**, **3**, and **4** and **4** are given in Table I. Those conditions which resulted in C–C

bond cleavage in the metallacyclopentanes also gave high yields of C–C bond cleavage products in the metallacyclohexanes. For example, the five-coordinate nickel complex **3** produced ethylene and $Ni(C_2H_4)(PPh_3)_2$ (**5**) as the major products.[4] The chemistry of this complex will be examined first.

+ $(Ph_3P)_2Ni(C_2H_4)$
5, 39% (based on 3)
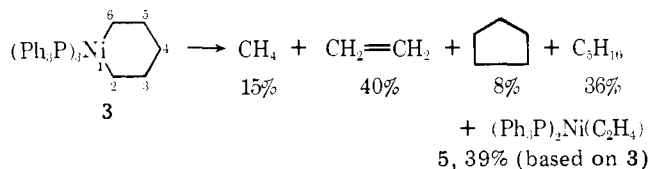
Either α- or β-C–C cleavage would result in the ultimate production of a carbenoid complex which could yield the observed products (Scheme I).

Scheme I
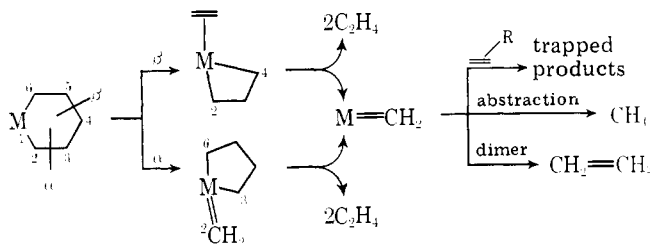
Based on past results β cleavage would be expected to be the major pathway of decomposition of metal alkyls; however the *α cleavage* route could be demonstrated to be the major route by deuterium labeling. Tris(triphenylphosphine)pentamethylenenickel(II)-*2,2,6,6-d_4* (**3b**) was prepared and allowed to decompose in the presence of cyclohexene. Up to 10% (per Ni)

3b   6
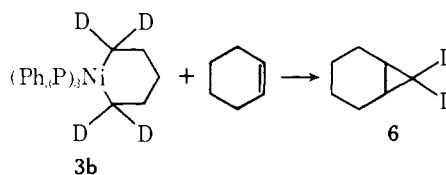
yields of norcarane (**6**) of high isotopic purity were isolated.[5] The isotopic purity decreased from 90 to 70% as the reaction progressed.[6] This suggested that the loss of isotopic purity was due to some competing reaction which moved the label from the 2,6 positions.[7] The fact that the isotopic purity was above 50% demonstrated that α-C–C bond cleavage occurred first. β cleavage would have given a maximum of 50% purity since a labeled carbon and an unlabeled carbon become equivalent in the intermediate resulting from β cleavage.[8] Other evidence for initial α-C–C bond cleavage was the lack of C_3 products

Table I. Decomposition Reactions of Metallacyclohexane Complexes[a]

| compds | reaction condition, °C, h | percent of decomposition products[b] | | | | | |
		CH_4	C_2H_4	C_3H_6	C_4H_8	c-C_5H_{10}	C_5H_{10}
$Ni(CH_2)_5(PPh_3)_3$ (**3a**)	23, 24	15	40	0	1	8	36
3a + PPh_3[c]		4	64	0	1	4	27
$Ni(CH_2)_5(PPh_3)_2$ (**2a**)		3	8	0	5	68	16
2a + PPh_3[c]		7	56	0	1	6	30
2a + $h\nu$[d]	0, 2	30	43[e]	5	5	15	0
$Ti(CH_2)_5Cp_2$ (**4a**)	23, 6	1	1	0	1	34[f]	63
4a + PR_3[g]		44	15	4	20	12[f]	5
4a + $h\nu$[h]	−40, 3	60	7	0	1	24[f]	8

[a] Decomposition reactions were performed in toluene solution for **2a**, **3a**, and decalin solution for **4a**. [b] Product gases were analyzed by GLC in the vapor phase as well as the solution phase. These were average values of several experiments. [c] Up to ten times excess triphenylphosphine was used. [d] Photolysis was performed in a quartz tube. During photolysis 54% of **2a** decomposed, while only trace acmounts of **2a** decomposed in the dark. Trisphosphine complex, **3a**, gave almost the same decomposition pattern as **2a**. [e] This value contains 46% ethane. [f] No cyclopentane was observed but n-pentane was observed. [g] Tertiary phosphines such as PEt_3, $P(n\text{-}Bu)_3$, PPh_3, or PCy_3 were used and each phosphine showed almost the same effect on the decomposition reaction of **4a**. [h] By photolysis 20% of **4a** decomposed but **4a** was stable at −40 °C in the dark.