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## ( $\pi$ -CYCLOPENTENYL)( $\pi$ -CYCLOPENTADIENYL)NICKEL: A NOVEL CATALYST FOR THE CONVERSION OF ETHYLENE TO 1-BUTENE AND n-HEXENES

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### Summary

( $\pi$ -Cyclopentenyl)( $\pi$ -cyclopentadienyl)nickel, ( $h^5$ -C<sub>5</sub>H<sub>5</sub>)Ni( $h^3$ -C<sub>5</sub>H<sub>7</sub>), is a novel, highly active, unicomponent catalyst for the conversion of ethylene to n-butenes and n-hexenes at 145–150°C. At high conversions of ethylene (70–90%), the dimeric product (80–86% yield) contains a high percentage (90–82%) of 1-butene. Experimental evidence is presented which strongly indicates that the cyclopentadienyl group remains bonded to the nickel during catalysis while the cyclopentenyl group is labile. A possible mode of activation is the reversible elimination of cyclopentadiene from ( $h^5$ -C<sub>5</sub>H<sub>5</sub>)Ni( $h^3$ -C<sub>5</sub>H<sub>7</sub>) to generate  $\pi$ -cyclopentadienylnickel hydride as a catalytically active intermediate. An improved synthesis of the title compound (70% yield) by direct hydrogenation of nickelocene is also reported.

### Introduction

Much interest has been shown in recent years in the use of Group VIII transition metal salts and complexes as catalysts for the homogeneous dimerization and oligomerization of ethylene. In 1965 Alderson [1] showed that the chlorides of rhodium and ruthenium catalyzed the dimerization reaction. At > 90% ethylene conversion, 2-butene was the major product (95–98% selectivity) with only 2–5% of 1-butene isolated. However, at low ethylene conversions (25–30%), obtained by employing low temperatures and short reaction times, the 1-butene selectivity could be increased somewhat to 38%. Ketley [2] later demonstrated that palladium chloride was also an effective catalyst for 2-butene (99% selectivity) production. Hata [3] reported that 2-butene (95% selectivity)

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was formed from ethylene in the presence of cobalt(III) acetylacetonate and aluminum alkyls. Yamamoto's report [4] that the complex  $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$  is active by itself for the dimerization of ethylene to 2-butene (98% selectivity) serves as one of very few examples in which the transition metal complex does not have to be activated by a Lewis acid co-catalyst.

By far the largest area of interest among Group VIII metals has been in the use of complex nickel catalysts for the homogeneous dimerization and oligomerization of ethylene. Wilke [5] showed that a catalyst prepared from  $\pi$ -allylnickel chloride and an aluminum halide promotes the dimerization of ethylene to 2-butene. Several other workers [6–12] have published results on the use of catalysts prepared from nickel compounds with aluminum alkyls, diethylaluminum ethoxide, alkylaluminum halides, and boron trifluoride etherate. This work has been extended by most of these authors by the addition to the catalyst of phosphines which generally have the effect of increasing the rate of dimer formation. However, in all cases, 2-butene was the major component (greater than 80%) in the dimeric product formed.

In these catalyst systems the authors have generally assumed that the nickel atom is the active dimerization center\*. In view of this presumably general mechanistic feature, it is surprising that there is only one example in the literature of a simple nickel compound in the absence of a Lewis acid (such as an alkylaluminum compound) which catalyzes the dimerization of ethylene. Tsutsui [13] has reported that dicyclopentadienylnickel (nickelocene) is a homogeneous catalyst for the conversion of ethylene to dimer high in 1-butene (89%) content. However, the nickelocene had a very low catalytic activity as only 3.0 g of dimer was obtained from 1.0 g of catalyst after 18 hours at 200°C. We have discovered [14] that  $(\pi\text{-cyclopentenyl})(\pi\text{-cyclopentadienyl})\text{nickel}$  ( $h^5\text{-C}_5\text{H}_5$ )Ni( $h^3\text{-C}_5\text{H}_7$ ), which is prepared in high yield by direct hydrogenation of nickelocene [15], is a highly active, highly selective, homogeneous catalyst for the conversion of ethylene to 1-butene and n-hexenes. Because of its unicomponent character ( $h^5\text{-C}_5\text{H}_5$ )Ni( $h^3\text{-C}_5\text{H}_7$ ) has been particularly amenable to mechanistic studies on the nature of its catalytic activity.

## Results

$(\pi\text{-Cyclopentenyl})(\pi\text{-cyclopentadienyl})\text{nickel}$  was first prepared [16, 17] in 18% yield by direct reaction of cyclopentadiene with nickel carbonyl in benzene solution. We have found that in the presence of a trace amount of Raney nickel initiator, ( $h^5\text{-C}_5\text{H}_5$ )Ni( $h^3\text{-C}_5\text{H}_7$ ) is obtained in 70% yield from the hydrogenation of nickelocene (70% conversion) in tetrahydrofuran solvent (nickelocene/RaNi = 100) at 45°C and 580 psi hydrogen pressure. At higher nickelocene conversions (90–95%), the yield of  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  decreases to about 50%. Wollensak [18] has previously reported that  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  is obtained in only 4% yield at 87% conversion of nickelocene by hydrogenation at 25°C and atmospheric pressure. The low yield observed by Wollensak presumably arises from the use of a low nickelocene/RaNi ratio (2.5) as well as from the use of ethanol as a solvent.

\* Jones [11], however, has proposed that dimerization catalysts prepared from nickel chloride and alkylaluminum compounds operate at least in part by a cationic reaction mechanism involving aluminum as the primary reaction center

TABLE 1

DIMERIZATION OF ETHYLENE.  $(C_5H_5)_2Ni$  vs  $C_5H_5NiC_5H_7$   
(554 mmol of ethylene and 20 g of benzene solvent)

Nickel compound (mmol)	Temp. (°C)	Time (h)	Conversion (%)	Yield (%)			Composition of butenes (%)		Linearity of hexenes (%)	Activity <sup>d</sup>
				C <sub>4</sub>	C <sub>6</sub>	C <sub>8</sub>	1-But-ene	2-But-ene		
$(C_5H_5)_2Ni^a$ (5.3)	200	18	13–20 <sup>c</sup>	>98	<2		89	11		0.2
$(C_5H_5)_2Ni^b$ (2.0)	150	0.5	2	>98	<2		95	5		1.5
$C_5H_5NiC_5H_7^b$ (2.0)	150	0.5	90	80	15	3	82	18	86	76
$C_5H_5NiC_5H_7^b$ (1.0)	150	0.75	72	86	12	2	88	12	87	80
$C_5H_5NiC_5H_7^b$ (1.0)	150	1.25	88	83	14	2	84	16	86	59

<sup>a</sup> Ref. 13. <sup>b</sup> This work. <sup>c</sup> It was estimated from the size of the reaction vessel and the ethylene pressure that about 800 mmol of ethylene was charged in this experiment. <sup>d</sup> [(g of products)/(g of catalyst × h)].

In Table 1 are summarized the results of several experiments in which the homogeneous reaction of ethylene with  $C_5H_5NiC_5H_7$  and nickelocene catalysts are compared. The activity of the  $C_5H_5NiC_5H_7$  catalyst is high [76–80(g of products)/(g of catalyst × h)] being at least 50 times greater than that of nickelocene under similar reaction conditions (150°C).<sup>\*</sup> The dimeric product (80–86% yield) contains a remarkably high percentage of 1-butene (82–88%) at high ethylene conversions (90–72%). In contrast to nickelocene, the  $C_5H_5NiC_5H_7$  catalyzed reaction affords appreciable amounts of hexenes (12–15% yield). 1-Hexene is the principal component (65%) of the hexene fraction. The total linearity (normal alkene content) of the C<sub>6</sub> fraction has been determined by hydrogenation to be 86%. Small amounts of octenes (2–3% yield) of 78% linearity (similarly determined) are also formed.

Some limited studies on the life of the  $C_5H_5NiC_5H_7$  catalyst have been carried out. With a high molar ratio of ethylene/catalyst (1000/1) the ethylene conversion is 70% (2 h at 150°C) and the 1-butene content of the dimer (86% yield) is 90%. At least 100 g of butenes and hexenes per g of catalyst is obtained. At the end of the reaction period, the activity of the catalyst, after repressuring with ethylene, is about half of that possessed initially.

The effect of several additives on the  $C_5H_5NiC_5H_7$  catalyzed reaction of ethylene has been examined (Table 2). The presence of diethylaluminum ethoxide (Et<sub>2</sub>AlOEt) reduces the 1-butene content of the dimer from 75% to 36% although the linearities of the C<sub>6</sub> and C<sub>8</sub> products are not significantly altered. Thus, the Et<sub>2</sub>AlOEt<sup>\*\*</sup> promotes the  $C_5H_5NiC_5H_7$  catalyzed isomerization of 1-butene to 2-butene. In the presence of an equimolar amount of triphenylphosphine (Ph<sub>3</sub>P) the ethylene conversion is reduced from 96 to 65% even with additional reaction

<sup>\*</sup> The  $C_5H_5NiC_5H_7$  catalyst is inactive below 130°C.

<sup>\*\*</sup> Et<sub>2</sub>AlOEt by itself only slowly catalyzes the isomerization of 1-butene to 2-butene at 150°C (5% conversion after 1 h)

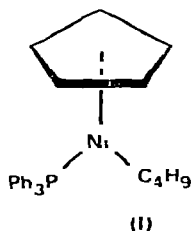
TABLE 2

EFFECT OF ADDITIVES ON  $C_5H_5NiC_5H_7$  CATALYZED REACTION OF ETHYLENE  
(536 mmoles of ethylene, 2 mmoles of  $C_5H_5NiC_5H_7$ , 20 g of benzene,  $150^\circ C$ )

Additive (mmol)	Time (h)	Conver- sion (%)	Yield (%)			Composition of butenes (%)		Linearity (%)	
			$C_4$	$C_6$	$C_8$	1-but- ene	2-but- ene	$C_6$	$C_8$
None	1.0	96	78	17	3	75	25	85	78
$Et_2AlOEt$ (3)	1.0	98	75	18	4	36	64	86	79
$Ph_3P$ (2)	2.0	65	88	7	2.5	91	9	95	85
$Bu_3P$ (2)	2.0	51	30	17	2	92	8	85	55
Pyridine (2)	1.0	94	78	17	3.5	60	40	80	70

time (Table 2). However, the linearities of the  $C_6$  and  $C_8$  products are increased to 95 and 85%, respectively. Tri-*n*-butylphosphine ( $Bu_3P$ ) lowers the conversion to 51% and also decreases the linearity of the  $C_8$  product to 55%. Pyridine does not significantly alter the ethylene conversion (94%) but does decrease the linearities of the  $C_6$  and  $C_8$  products to 80 and 70%, respectively.

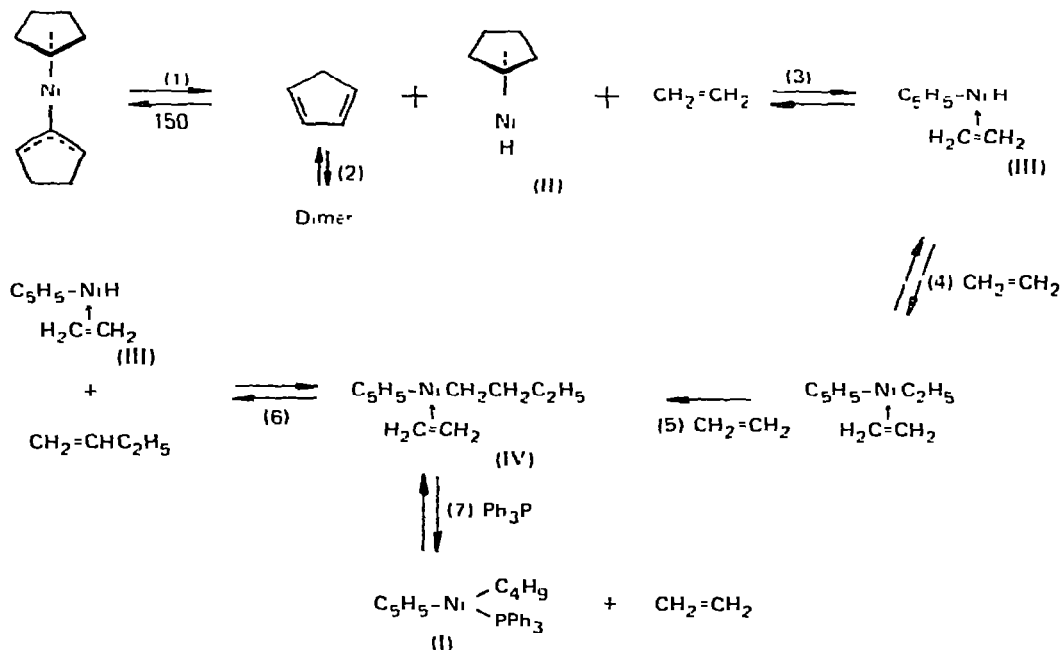
A number of experimental observations have been made which bear on the mechanism of the reaction of ethylene with the  $C_5H_5NiC_5H_7$  catalyst: (1) Introduction of a benzene solution of  $C_5H_5NiC_5H_7$  into a GLC column at  $150^\circ C$  produces cyclopentadiene in 7% yield (based on  $C_5H_5NiC_5H_7$  introduced) and 3% dicyclopentadiene. By raising the temperature of the column to  $200^\circ C$ , at least 85% of the  $C_5H_5NiC_5H_7$  introduced is recovered. (2) Elution chromatography (alumina) of a reaction product mixture (96% ethylene conversion) affords a 50% recovery of the  $C_5H_5NiC_5H_7$  initially charged. Several other chromatographic fractions are obtained in small amounts but none of them could be completely identified. However, in most of these fractions the NMR spectra show that the resonances [15] at  $\delta = 5.0$  and 3.8 ppm due to the  $\pi$ -cyclopentenyl allylic hydrogens have disappeared. With all of the chromatographic fractions the resonance at 5.2 ppm due to the cyclopentadienyl group is retained. (3) Elution chromatography of the product mixture from an experiment with both  $C_5H_5NiC_5H_7$  and  $Ph_3P$  present affords a 25% yield of a compound whose NMR spectrum is identical with that of authentic (*n*-butyl)( $\pi$ -cyclopentadienyl)(triphenylphosphine)nickel [19, 20] (I). Reaction of 1.0 mmole of I with 400 mmoles of ethylene in benzene solvent



at 150–175°C gives a 15–20% conversion of ethylene to dimer (97% 1-butene). (4) The hydrogenated product from a typical oligomerization experiment contains ethylcyclopentane (20% yield based on  $C_5H_5NiC_5H_7$  charged) as well as cyclopentane.

## Discussion

The results strongly suggest that the cyclopentadienyl group remains bonded to the nickel during catalysis while the  $\pi$ -cyclopentenyl group is labile. One possible mode of activation of  $C_5H_5NiC_5H_7$  is the reversible elimination of cyclopentadiene (step 1) to generate  $\pi$ -cyclopentadienylnickel hydride\* (II). Ethylene may assist in driving this elimination forward (i.e., steps 1 and 3 may be concerted) but a more important driving force is the dimerization of cyclopentadiene (step 2). The results observed upon the introduction of  $C_5H_5NiC_5H_7$  into a GLC column at 150°C are consistent with the occurrence of such an elimination process (step 1). The activation step 1 is especially attractive since the reversible nature of steps 1, 2 and 3 accounts for the recovery of a high (50%) percentage\*\*



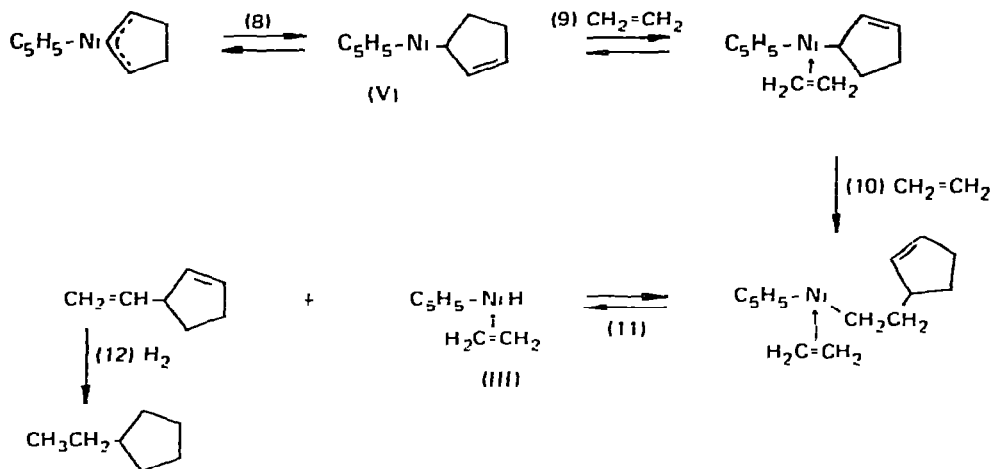
of  $C_5H_5NiC_5H_7$  from the product mixture. Once intermediates II and III have arisen, the formation of 1-butene is straight-forward. Insertion of  $\pi$ -bonded ethylene into the nickel hydrogen bond (step 4) is followed by insertion of  $\pi$ -bonded ethylene into the nickel carbon sigma bond (step 5) and elimination (step 6) to regenerate III. Intermediate IV may be trapped by reaction with triphenylphosphine (step 7) and this accounts for the isolation of product I when

\* Jonas and Wilke [21] have prepared (tricyclohexylphosphine)( $\pi$ -cyclopentadienyl)nickel hydride by reaction of bis(tricyclohexylphosphine)nickel with cyclopentadiene.

\*\* It is also possible that 50% of the  $C_5H_5NiC_5H_7$  never enters the catalytic cycle.

the reaction is carried out with  $\text{Ph}_3\text{P}$  present. However, IV may also react with more ethylene to give an insertion product which affords 1-hexene and III via elimination.

A second possible mode of activation of  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  involving insertion of  $\pi$ -bonded ethylene into the metal carbon sigma bond of the  $\sigma$ -allyl form<sup>\*</sup> (V) of  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  (steps 9 and 10) followed by elimination of 3-vinylcyclopentene (step 11) would also generate II or its catalytic equivalent III. 3-Vinylcyclopentene would afford ethylcyclopentane on hydrogenation. Since ethylcyclopentane is, indeed, isolated in 20% yield it would appear that at least 20% of the  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  catalyst is activated in this manner.



1-Butene must enter the coordination sphere of the catalyst in order to be isomerized\*\* to 2-butene. The small percentage of 2-butene formed is attributed to the strong preference which either II or III has for coordination with ethylene rather than 1-butene. In the presence of diethylaluminum ethoxide ( $\text{Et}_2\text{AlOEt}$ ), complex formation [11] between II and the aluminum species may



occur to give VI or VII. The coordination of the  $\text{Et}_2\text{AlOEt}$  to the nickel may increase the reactivity of the nickel complex to 1-butene, and hence, promote the isomerization of 1-butene to 2-butene. The effect which added  $\text{Et}_2\text{AlOEt}$  has on the 1-butene content of the dimer offers an explanation of why other workers [6-12] found such a low 1-butene content with catalysts prepared from various nickel compounds and alkylaluminum components.

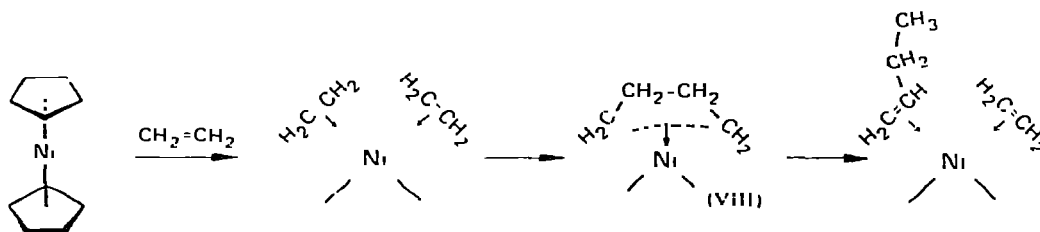
The observation that the triphenylphosphine substituted complex I is a much less active catalyst than  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  is readily rationalized. Thus, the

\* Complex V may also undergo elimination to give II and cyclopentadiene.

\*\* Tolman [22] has discussed the mechanism of the isomerization of 1-butene to 2-butene using an hydridic nickel catalyst, tetrakis(triethylphosphite)nickel hydride.

postulated intermediate II is coordinatively unsaturated and is, thereby, provided with a strong driving force for coordination with ethylene. On the other hand, I already has the rare gas configuration\* and, consequently, has no special driving force for reaction with ethylene. It appears probable that at least part of the  $\text{Ph}_3\text{P}$  remains bonded to the nickel during catalysis since it participates in the determination of the nature of the products (improved linearity in the  $\text{C}_6$  and  $\text{C}_8$  fractions).

In order to explain the nickelocene catalyzed dimerization of ethylene, Tsutsui [13] has proposed a three step mechanism, the first step of which involves displacement of the cyclopentadienyl rings by two molecules of ethylene. The second step is coupling of the two ethylene molecules on the nickel followed by the simultaneous shift of a hydrogen radical and the bonding of another ethy-



lene to the metal. The nature of the bonding of the butyl fragment to the Ni in intermediate VIII has not been made clear nor has a mechanism for the migration of the hydrogen radical been offered. McBride and Stone [24] have reported that nickelocene reacts with ethylene at  $70^\circ\text{C}$  to give  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  in 2.5% yield. Since we have demonstrated that  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$  is 50 times more active than nickelocene for dimerizing ethylene, the low activity of the nickelocene can be accounted for by the "in situ" formation of a small amount of  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$ . Accordingly, we propose that the actual catalytic species involved in Tsutsui's nickelocene catalyzed dimerization of ethylene is  $\text{C}_5\text{H}_5\text{NiC}_5\text{H}_7$ .

## Experimental section

### *( $\pi$ -Cyclopentenyl)( $\pi$ -cyclopentadienyl)nickel*

A mixture of 10 g of nickelocene (Strem, purified by recrystallization from toluene), 0.1 g of Raney nickel and 100 ml of dry tetrahydrofuran in a 300 ml Magne-drive autoclave was stirred under 580 psi hydrogen pressure. Uptake of hydrogen commenced after two min. at  $45$ – $48^\circ\text{C}$  and within 10 min. 1.0 mol of hydrogen per mol of nickelocene was absorbed. The hydrogenation was terminated by rapid cooling to  $0^\circ\text{C}$  with ice-water.

In the nitrogen box the reaction mixture was filtered and the filtrate concentrated under reduced pressure to give 8.0 g of residue. After trituration with 18 ml of *n*-pentane, the mixture was filtered to remove 3.0 g (70% conversion) of crude nickelocene, m.p.  $150$ – $160^\circ\text{C}$ . Removal of pentane from the filtrate afforded 5.0 g of red-brown crystals, m.p.  $50$ – $57^\circ\text{C}$ . The purity of the ( $\pi$ -cyclo-

\* Tolman [23] has discussed the importance of 16- and 18-electron organometallic complexes as intermediates in homogeneous catalysis.

pentenyl)( $\pi$ -cyclopentadienyl)nickel (70% yield) was estimated by thin-layer chromatography to be 90–95% with nickelocene being the impurity. Samples of 99% purity were prepared by recrystallization from pentane followed by high vacuum (0.01 mm) sublimation at 50°C. The red-brown crystals melted at 53–55°C which is 10°C higher than that reported by Fischer [16], Dubeck [17] or Wollensak [18].

*Ethylene with ( $h^5$ -C<sub>5</sub>H<sub>5</sub>)Ni( $h^3$ -C<sub>5</sub>H<sub>7</sub>) catalyst*

In a nitrogen dry box 0.37 g (2 mmol) of ( $h^5$ -C<sub>5</sub>H<sub>5</sub>)Ni( $h^3$ -C<sub>5</sub>H<sub>7</sub>) and 20 g of benzene were charged to an 85 ml Inconel autoclave equipped with magnetic stirring. Outside the dry box at –60°C under nitrogen, 15.5 g (554 mmol) of ethylene was added to the autoclave. The reactor was stirred at 145–150°C for 0.5 h. Unreacted ethylene was vented slowly at –60°C to –10°C. Gas liquid chromatographic analysis of the liquid product (32.5 g) on a 20 ft column packed with 15% SE-30 on Chromosorb-W at 50–200°C showed the presence of 11.1 g of dimer (82% 1-butene, 18% 2-butene), 2.3 g of trimer, 0.3 g of tetramer and 0.2 g of pentamer. Benzene solvent served as an internal reference for the analysis. GLC analysis on a 200 ft squalane capillary column at 30°C showed that 1-hexene was the principal component (65%) of the trimer fraction.

The product mixture was washed with 10% sulfuric acid at 0°C and then three times with ice-water. Following drying (Drierite), the treated product and 0.5 g of 10% palladium-on-carbon were stirred at 25–75°C under 400 psi hydrogen pressure for two hours. GLC analysis showed that the C<sub>6</sub> and C<sub>8</sub> fractions contained 86% n-hexane and 78% n-octane, respectively. The presence of 0.04 g (20% yield) of a compound whose retention time was identical with that of ethylcyclopentane was also demonstrated. The ethylcyclopentane was isolated in a pure form by a combination of fractional distillation and GLC trapping and identified by comparison of its mass spectrum with that of an authentic sample.

*Recovery of ( $\pi$ -cyclopentenyl)( $\pi$ -cyclopentadienyl)nickel catalyst*

In an experiment similar to that described above 0.74 g (4 mmol) of C<sub>5</sub>H<sub>5</sub>NiC<sub>5</sub>H<sub>7</sub> was treated with 550 mmol of ethylene in 20 g of benzene solvent (1 h at 135–150°C). About 97% of the ethylene was converted to oligomers. The product mixture was filtered in the nitrogen dry box to remove 0.025 g of insoluble material. Solvent and volatile products were removed from the filtrate by distillation in vacuo at 25°C. The residue in hexane was placed on a chromatographic column containing 200 g of Woelm activity grade 1 alumina (dry box). The column was eluted with hexane containing increasing percentages of benzene. With 40–50% benzene a fraction containing 0.37 g (50% recovery) of a red-brown solid whose NMR spectrum was essentially identical with that of the C<sub>5</sub>H<sub>5</sub>NiC<sub>5</sub>H<sub>7</sub> catalyst was obtained. A number of other fractions were obtained using 10–30% benzene but the quantities isolated were insufficient for complete characterization (see Results section).

*Ethylene with C<sub>5</sub>H<sub>5</sub>NiC<sub>5</sub>H<sub>7</sub>/Ph<sub>3</sub>P*

In the nitrogen dry box, 0.74 g (4 mmol) of C<sub>5</sub>H<sub>5</sub>NiC<sub>5</sub>H<sub>7</sub>, 1.05 g (4 mmol) of triphenylphosphine and 20 g of benzene were charged to the 85 ml Inconel autoclave. Outside the dry box at –60°C under nitrogen 15.0 g (536 mmol) of



ethylene was added to the autoclave. The reactor was stirred at 145–150°C for 1 h. GLC analysis of the liquid product showed 7.9 g of dimer (92% 1-butene), 0.63 g of trimer and 0.3 g of higher oligomers.

Inside the dry box the product mixture was filtered to remove 0.05 g of insoluble material. Solvent and volatile products were removed from the filtrate by vacuum distillation at 25°C. The residue dissolved in 5 ml of benzene was placed on a chromatographic column containing 200 g of Woelm activity grade 1 alumina (dry box). The column was eluted with hexane containing increasing percentages of benzene. With 50% benzene a fraction containing 0.44 g (25% yield) of a greenish-brown solid was obtained. The NMR spectrum in deuterobenzene showed two singlets at  $\delta$  7.8 ppm and 7.1 ppm (*o*-, *p*- and *m*-hydrogens of  $C_6H_5$ ), a singlet at 4.85 ppm ( $C_5H_5$ ) and an unresolved broad peak at 0.5–0.2 ppm ( $C_4H_9$ ); the relative areas of the peaks were 15/5/9. The spectrum was identical with an authentic sample of  $C_5H_5Ni(Ph_3P)(C_4H_9)$  prepared by reaction [19, 20] of  $C_5H_5NiCl(Ph_3P)$  with *n*- $C_4H_9MgBr$ .

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