A New Nickel Complex for the Oligomerization of Ethylene

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We report the synthesis of $(\eta^3\text{-}C_8H_{13})((C_6H_5)_2PCH_2COO)Ni$ (1), which proved to be an excellent one-component model catalyst for the oligomerization of ethylene as practiced in Shell's higher olefin process (SHOP). In toluene solution this complex exists in two isomeric forms, the C_8H_{13} ligand being 60% 4-enyl and 40% η^3-allyl. Under reaction conditions (75 °C, 10–80 bar, ethylene in toluene) 1 catalyzed the highly selective oligomerization of ethylene to linear (99+%), α olefins (93–99%) at activities of 0.6 mol of ethylene/mol of Ni/s. The chain growth factor K ranges from 0.67 to 0.77 depending on reaction conditions. Kinetic activation parameters and reaction constants could be determined (E_a = 71 kJ mol^{-1}; $S^{\ddagger} = -49$ J mol^{-1} K^{-1}; $k_{\text{insert.}/348\text{K}}$ = 0.81 s^{-1}).

I. Introduction

The industrial manufacture of α olefins in the C_8–C_{20} range is of substantial technical interest to provide olefins for detergents, plasticizers, lubricants, oil additives, and a variety of fine chemicals. Recently, Shell developped a new ethylene oligomerization process, SHOP, which was discovered by W.K. and which is practiced worldwide in various plants.[1] This process is characterized by a remarkable selectivity. Chelating ligands are responsible for the high selectivity, which is needed to combine oligomerization and metathesis in the process scheme.[2]

The majority of papers dealing with homogeneous transition-metal catalysts relate to monodentate ligands, primarily tertiary phosphines. The effect of chelates has found only scattered interest. This is surprising, when considering the impact chelating ligands play in nature.

In our search to understand the reaction mechanism of ethylene oligomerization, we prepared the complex $(\eta^3\text{-}C_8H_{13})((C_6H_5)_2PCH_2COO)Ni$ (1) that contains a P,O chelate. Compound 1 showed high activity and selectivity in the SHOP reaction.

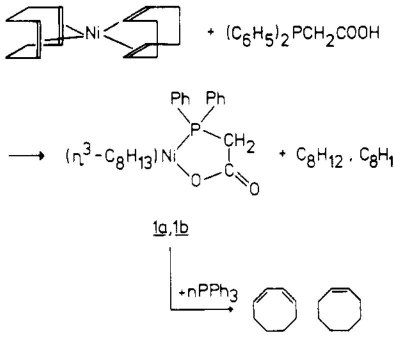
In this paper we give an account of the preparation of 1 and its catalytic performance.

II. Experimental Section

All experiments were carried out in an argon atmosphere and with dry solvents.[3]

Preparation of $(\eta^3\text{-}C_8H_{13})((C_6H_5)_2PCH_2COO)Ni$ (1). A 18-mmol sample of $(COD)_2Ni$[4] (COD = cyclooctadiene) and 14 mmol of $(C_6H_5)_2PCH_2COOH$[5] are dissolved in 100 mL of toluene. After 1-h reaction at room temperature, the solvent is distilled off at 10^{-2} torr. GC analysis shows that the distillate contains about 8 mmol of cyclooctadiene isomers. The dry residue is dissolved in a mixture of 100 mL of toluene and 100 mL of n-hexene. Unreacted $(COD)_2Ni$ precipitates at −30 °C and is filtered off. To the clear solution are successively added 50 mL of n-hexane and 100 mL of n-octane. After several days burgundy red crystals of 1 are formed. Recrystallization from a mixture of toluene, hexane, and octane yields 6.3 mmol of $(\eta^3\text{-}C_8H_{13})((C_6H_5)_2PCH_2COO)Ni$ (1) in large tetragonal crystals ($a = b$ = 2.51 nm, c = 2.79 nm), mp 214–216 °C. Elemental analysis and chemical decomposition of 1 by added triphenylphosphine proved that the compound contains 1 mol of C_8H_{13} per mol and about 20% toluene and octane as crystal liquid solvent and free 1 could not be obtained. Spectroscopic characterization included MS, IR and ^{1}H, ^{13}C, and ^{31}P NMR: MS (70 eV, chemical ionization with isobutene, 210 °C), m/e 243 (phosphinoacetic acid), 109 (C_8H_{13}); IR (KBr, cm^{-1}) ν(C–H) 3050, 2920, 2860, 2810, ν(C=O) 1580, ν(C–O) 1375, ν(C–C(arom)) 1480, 1430, ν(P–C(arom)) 1100, 1085, ν(P–C(aliph)) 735; ^{31}P NMR (109.32 MHz, in C_6D_6, external standard 85% H_3PO_4) one signal at −2.6 ppm vs. −15.4 ppm for pure $(C_6H_5)_2PCH_2COOH$; ^{1}H and ^{13}C NMR spectral data are shown in Table I (1 was recrystallized from toluene-d_8). ESCA, K edge X-ray absorption spectra,[6] and X-ray structure analysis are to be published in a later paper.

Scheme I



The discontinuous kinetic experiments were carried out by using 75-mL, V4A, stainless-steel batch autoclaves equipped with magnetic stirrers. Under an argon blanket they were charged with a toluene solution of 1, toluene, n-heptane as the GC standard, and ethylene, adding up to a total of 40 mL (at 25 °C). After a fast heatup to the desired temperature the pressure drop due to the catalytic reaction could be followed by means of a manometer. Through independent determination of the P–T function of various toluene/ethylene mixtures the measured P–T curves, as shown in Figure 1, could be calibrated as concentration over time, which finally yield absolute rates of reaction and turnover numbers N. The oligomer products were analyzed after a total reaction time of 35 min by capillary gas chromatography (Carlo Erba 2200; silicon OV 101, 60 m × 0.25 mm i.d. WGA Duesseldorf; temperature progression 6 min, isothermal at 30 °C, 8°/min heatup, isothermal at 230 °C).

III. Results and Discussion

A. The Catalyst. When bis(cyclooctadiene)nickel was reacted with (diphenylphosphino)acetic acid, complex 1

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(1) (a) Keim, W., et al. (Shell Dev.) U.S. Patents 3 635 937, 3 647 914, 3 686 159, 3 644 563, 3 647 914, 1972. (b) *Eur. Chem. News* Apr 5, **1982**, 26; Jan 26, **1981**, 27; Jul 6, **1981**, 23; Feb 11, **1980**, 27.

(2) Freitas, E. R.; Gum, C. R. *Chem. Eng. Prog.* **1979**, *75*(1), 73–76.

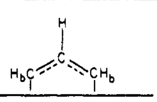
(3) Peuckert, M. Thesis Rheinisch-Westfälische Technische Hochschule Aachen, Aachen, West Germany, 1980.

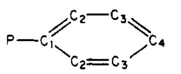
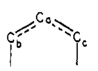
(4) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5–9.

(5) (a) Issleib, K.; Thomas, G. *Chem. Ber.* **1960**, *93*, 803–808. (b) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490–1494.

(6) Peuckert, M.; Weber, R. S.; Storp, S.; Keim, W., accepted for publication in *J. Mol. Catal.*

Table I. ^1H NMR and ^{13}C NMR Spectral Data of $(\eta^3\text{-}C_8H_{13})((C_6H_5)_2PCH_2COO)Ni$ (1)[a]

	C_6H_5P							
^1H NMR[b]	o-H	m,p-H	CH=CH	H_a	H_b	C-CH_2-C	P-CH_2-COO	Ni-C-CH
δ[c]	7.77 m	7.10 m	5.80 m	4.5 d	3.67 t	2.68 m[d] 2.4 m 1.6 m	1.37 s	0.17 m −0.45 d
integration	4	6	1.3	0.55	1.1	8.7	2	0.7 0.7

									
^{13}C NMR[b]	COO	C_4	C_2	C_1	C_3	C_a	C_b	C_c	CH
δ	178	137.6	132.4	128	125.4	112	88	79	40-14

[a] Complex 1 recrystallized from toluene-d_8. [b] Solvent C_6D_6, external standard Me_4Si. [c] Multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet. [d] Only main signals are listed, between 2.9 and 1.0 many methylene signals.

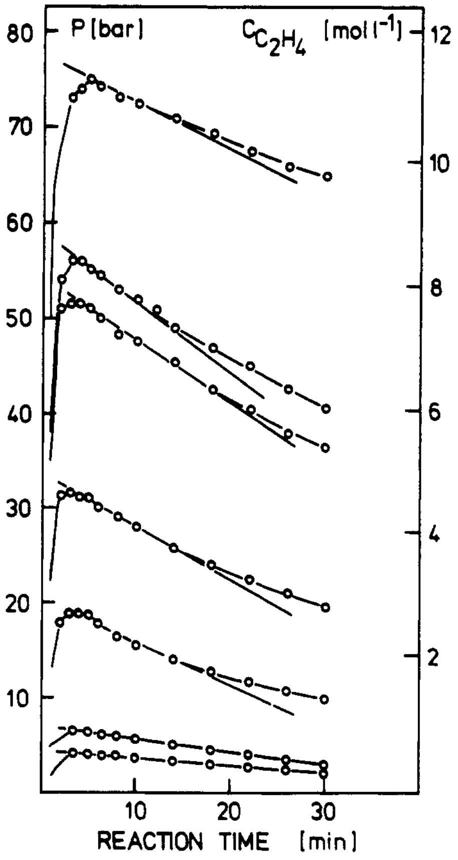
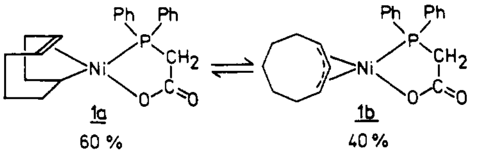


Figure 1. Pressure–time curves for the oligomerization of ethylene with catalyst 1 in toluene at 75 °C (Table II, experiments 1–7).

was obtained as shown in Scheme I. One cyclooctadiene ligand in $(COD)_2Ni$ is displaced by the $(C_6H_5)_2PCH_2COO^-$ moiety as a mixture of 1,3-, 1,4-, and 1,5-cyclooctadiene, bicyclo[3.3.0]oct-2-ene, and cyclooctene. The remaining C_8H_{13} group in 1 is formed via addition of the acidic hydrogen of Ph_2PCH_2COOH to the second 1,5-cyclooctadiene ring.

Though 1 is easily recrystallized from toluene/alkane mixtures and one always measures identical spectra of the substrate (see Experimental Section), the ^1H NMR spectrum (as well as the ^{13}C NMR) at first sight is somewhat puzzling (Table I). The relative intensities of aromatic to nonaromatic signals are 10:15 as expected. The two acetato methylene protons at 1.37 ppm are easily identified, but integration of the remaining signals leads to constant and reproducible but noninteger relations. These findings are interpreted as an equilibrium between the two isomeric forms 4-enyl **1a** and η^3-allyl **1b** at a ratio of 3:2.[7-9]



Characteristic for the 4-enyl isomer are the two signals about 0 ppm and the olefin signal at 5.80 ppm. Typical allyl signals (integration 1:2) appear at 4.5 and 3.67 ppm.[10,11] Since the 4-enyl to π-allyl ratio was foound to stay constant through repeated recrystallization procedures of 1, the question arises, whether in the solid state both isomers exist or only **1a** exists that then quickly equilibrates in solution. This point—though not bearing much importance for the catalysis—will be clarified by X-ray structure analysis.

The facile transformation of the 4-enyl structure **1a** into the π-allyl form **1b** is quite noteworthy and is in sharp contrast to the generally observed stability of Ni and Co complexes with O,O chelate ligands.[12] On the other hand, almost complete 4-enyl-to-η^3-allyl isomerization has been reported for the reaction of $(C_8H_{13})Ni(acac)$ with more basic σ donor ligands as for example C_2H_5SH and $P(OC_6H_5)_3$.[13] This illustrates the different behavior of O,O and O,P chelate complexes.

B. Catalytic Performance. In conformity with widespread usage, complex 1 so far has been referred to as the "catalyst". From a kinetic point of view this is not quite correct, as the term "catalyst" should rather be ascribed to the "active species".

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(7) Fischer, E. O.; Werner, H. *Z. Chem.* **1962**, *2*, 174–178.

(8) Wilke, G. et al. *Angew. Chem.* **1966**, *78*, 157–172.

(9) Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 155–173.

(10) (a) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1979**, 3536–3543. (b) Mann, B. E.; Pietropaolo, R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 2390–2393. (c) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.

(11) Barnett, K. W. *J. Organomet. Chem.* **1970**, *21*, 477–485.

(12) Keim, W.; Hoffmann, B.; Lodewick, R.; Peuckert, M.; Schmitt, G.; Fleischhauer, J.; Meier, U. *J. Mol. Catal.* **1979**, *6*, 79–97.

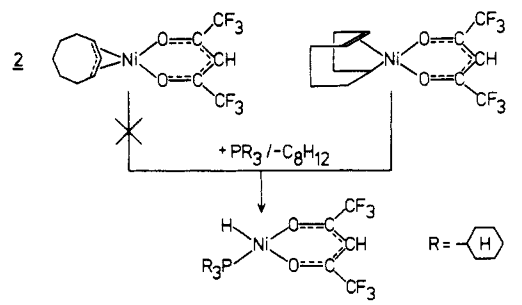
(13) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel", Academic Press: New York, 1974; Vol. 1.

Table II. Results of Batch Oligomerization of Ethylene with Catalyst 1[a]

expt	T, °C	$c_{C_2H_4}$, mol L^{-1}	$10^{-3}c_{cat.}$, mol L^{-1}	conversn, %	N, s^{-1}	linear, %	$\bar{\alpha}$ portion in C_4-C_{24}, %	β C_{10}-C_{20}
1	75	0.38	2.3	53	0.14	99+	99+	0.39
2	75	0.83	2.53	59	0.23	99+	99+	0.30
3	75	2.41	2.34	50	0.47	99+	99	0.29
4	75	4.72	2.47	41	0.57	99+	97	0.29
5	75	7.00	2.70	32	0.62	99+	98	0.30
6	75	8.95	3.39	30	0.57	99+	95	0.34
7	75	11.22	2.64	15	0.48	99+	96	0.50
8	75	4.58	0.99	24	0.71	99+	98	0.24
9	75	4.22	5.00	65	0.53	99+	93	0.37
10	60	4.83	2.27	9	0.17	99+	99+	0.16
11	85	4.95	2.29	62	1.12	99+	99+	0.10
12	95	4.75	2.32	69	1.83	99+	99+	0.10
13[b]	75	5.01	1.93	25	0.65	99+	99	0.27

[a] Solvent toluene; capillary GC analysis after 35-min total reaction time. [b] Addition of 1.67 mol L^{-1} 1-hexene.

Scheme II



After ethylene in slight stoichiometric excess was added to a solution of **1a**/**1b** at 75 °C, 20% bicyclo[3.3.0]oct-2-ene (via intramolecular insertion of the 4-enyl), 7% 1,5-cyclooctadiene, 34% 1,4-cyclooctadiene, 8% 1,3-cyclooctadiene, and 31% cyclooctene were detected by GC analysis. One is tempted to assume that the 61% of bicyclo[3.3.0]oct-2-ene, and 1,5- and 1,4-cyclooctadiene stem from **1a**, whereas the 39% of 1,3-cyclooctadiene and cyclooctene originate from **1b**. Relevant to this displacement is a recent finding in our laboratory.[14] We could isolate the isomeric complexes **2** and **3** (Scheme II). No equilibrium such as **1a** ⇄ **1b** could be observed for **2** and **3**. Most remarkably, **3** is an excellent catalyst for the oligomerization of 1-butene. Complex **2** is practically inactive. This can be understood when considering the ease of nickel hydride formation from **2** and **3** via elimination of C_8H_{12} (Scheme II). Upon reaction of **3** with tricyclohexylphosphine, a nickel hydride complex could be isolated.[15] Identical experiments with **2** failed.

All attempts to convert **1** to a Ni–H complex by adding R_3P were not successful. However, the quantitative displacement of the second C_8 ring occurred.

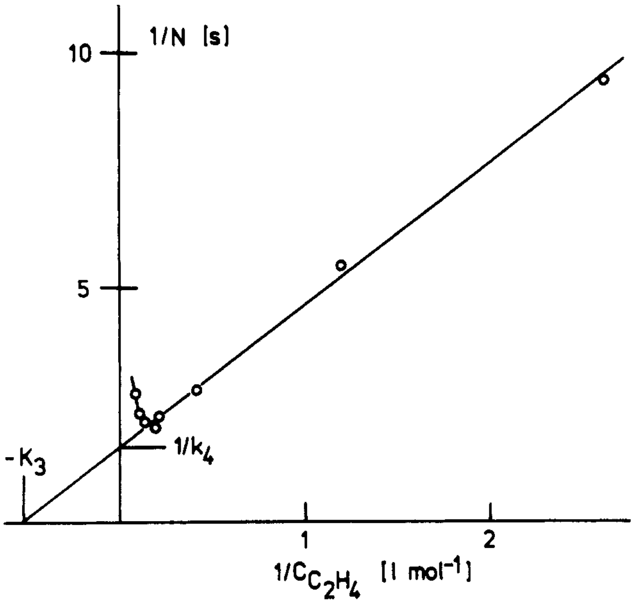


Figure 2. Lineweaver–Burk diagram for experiments 1–7 (Table II): reciprocal turnover numbers vs. $1/[C_2H_4]$.

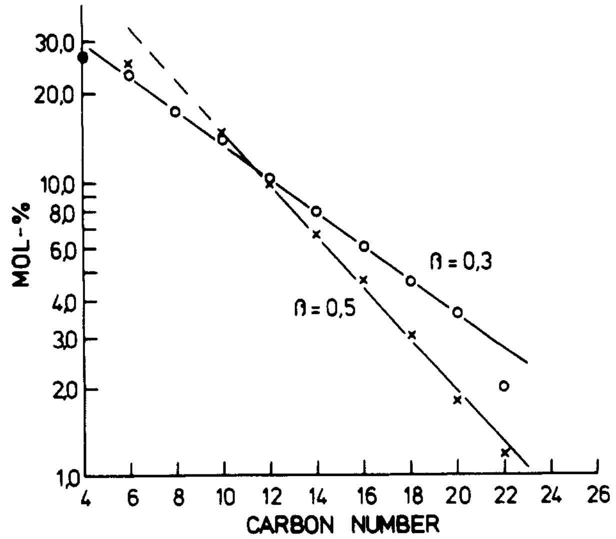


Figure 3. Schulz–Flory type oligomer distribution (Table II, experiments 2 and 7). The β values 0.3 and 0.5 correspond with K factors of 0.77 and 0.67, respectively.

The isolation of a nickel hydride complex would have been of interest in view of mechanistic consideration shown in Figure 4. A widely accepted mechanism for olefine oligomerizations invokes metal hydrides as active species,[16-18] thus isolation of a Ni–H complex could have been further support for a hydride mechanism. During the startup reaction of **1** with ethylene, a set of three high-field ^1H NMR signals (0.7, 0.15, and −0.5 ppm) evolved, which is characteristic of a nickel-alkyl group. Initial nickel-hydride formation as the activation step followed by re-

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(14) Kraus, G. Thesis Rheinisch-Westfälische Technische Hochschule Aachen, Aachen, West Germany, 1982.

(15) Despeyroux, B.; Lodewick, R.; Keim, W. *Compend. Erdöl Kohle Erdgas Petrochem.* **1981**, *Bd. 80/81*, 123–125.

(16) Langer, A. W. *J. Macromol. Sci. Chem.* **1970**, *A4*, 775–787.

(17) (a) Henrici-Olivé, G.; Olivé, S. *Adv. Polym. Sci.* **1974**, *15*, 1–30. (b) *Top. Curr. Chem.* **1976**, *67*, 107–127.

(18) Henrici-Olivé, G.; Olivé, S. "Monographs in Modern Chemistry", Verlag Chemie: Weinheim, 1977; Vol. 9.

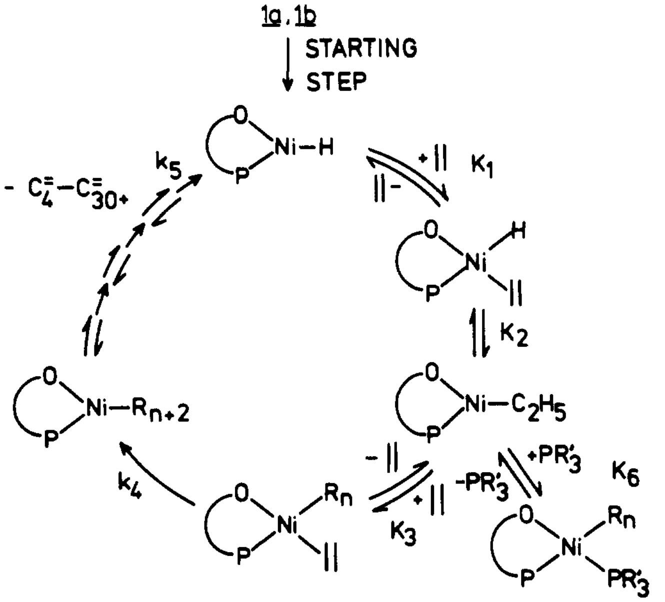

Figure 4. Simplified mechanism proposed for ethylene oligomerization with nickel O,P chelate complexes like 1 and the SHOP catalyst.

action with ethylene to form a nickel alkyl—as shown in Figure 4—can be supposed.

In Figure 1 and Table II the results of the oligomerization experiments are summarized. After the autoclaves are charged at room temperature and immersed into a heat bath, thermal equilibrium is reached within 3–5 min, upon which the catalytic reaction commences immediately as recorded by the pressure drop. At 25 °C 1 shows no activity. From the initial rates specific turnover numbers N (mol of ethylene per mol of Ni per s) are calculated. The rate is first-order in catalyst concentration (experiments 4, 8, and 9). Plotting $1/N$ over reciprocal ethylene concentration results in a straight line (Figure 2); only at very high concentrations of C_2H_4 is a deviation observed, probably due to a solvent effect of the substrate itself. This so-called Lineweaver–Burk diagram is in good agreement with the proposed Michaelis–Menten-type mechanism (Figure 4): association constant $K_3 = 0.52$ L mol^{-1} and $k_4 = 0.81$ s^{-1} being the rate constant of the rate-determining step in the rate law for the oligomerization.

$$r_{\mathrm{olig}} = [\mathrm{Ni}^*]\,\frac{k_4K_3[\mathrm{C_2H_4}]}{1 + K_3[\mathrm{C_2H_4}]}$$

$[\mathrm{Ni}^*]$ = catalyst concentration

Activation energy and entropy were determined (experiments 4 and 9–12) as $E_a = 71$ kJ mol^{-1} and $S^{\ddagger} = -49$ mol^{-1} K^{-1}.

So far we have just focused on the activity of 1. The selectivity is also listed in Table II. The oligomers are practically 100% linear and the α olefin content ranges from 93% to 99+%. This underlines the remarkable selectivity of 1 for ethylene only. To investigate the possibility of cooligomerization, we added 1-hexene and propylene (experiment 13). No branched or odd carbon number products could be found.

The chain length distribution is of the Schulz–Flory-type and can best be described by the β value (Figure 3).[19,20] That is the ratio between the rate r_{elim} of the chain growth terminating step and the rate r_{olig} of the propagation step. This is exemplified in Figure 4 by step 4 and step 5.

$$\beta = \frac{r_{\mathrm{elim}}}{r_{\mathrm{olig}}} = \frac{k_5(1 + K_3[\mathrm{C_2H_4}])}{k_4K_3[\mathrm{C_2H_4}]} \approx \frac{1}{TP}$$

Since the β values are determined only at the end of each run at high conversion, the steady-state condition is not strictly obeyed and a numerical analysis of our experiments seems difficult. Another molar growth factor often used to characterize the product composition is defined as

$$K = \frac{\text{mol fraction } \mathrm{C}_{n+2}\text{-alkene}}{\text{mol fraction } \mathrm{C}_n\text{-alkene}} = (1 + \beta)^{-1}$$

For an average $\beta = 0.3$ the K factor equals 0.77.[2]

Whereas the influence of the substrate concentration on the chain length is rather weak, there is a pronounced increase of the β value caused by addition of phosphine to the reaction mixture. Our proposed mechanism (Figure 4) therefore has to be completed by the equilibrium K_6, and β is then given by

$$\beta = \frac{k_5(1 + K_6[\mathrm{PR_3}] + K_3[\mathrm{C_2H_4}])}{k_4K_3[\mathrm{C_2H_4}]}$$

Acknowledgment. We thank Deutsche Forschungsgemeinschaft for supporting this work. We are grateful to Mrs. M. Sistig and Dr. W. Meltzow for assistance with the spectroscopic and analytical work.

Registry No. **1a**, 84108-24-7; **1b**, 84099-45-6; $(C_6H_5)_2PCH_2COOH$, 3064-56-0; ethylene, 74-85-1; bis(1,5-cyclooctadiene)nickel, 1295-35-8.

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(19) (a) Schultz, G. V. *Z. Phys. Chem., Abt. B* **1935**, *30*, 379–398. (b) *Ibid.* **1939**, *43*, 25–46.

(20) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561–1565.