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# METAL COMPLEXES IN CATALYTIC OLEFIN TRANSFORMATIONS.

2. STRUCTURE OF PHOSPHINE LIGANDS ATTACHED TO SILICA;

Ni-CATALYSTS FOR ETHYLENE DIMERIZATION

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 $\gamma$ -Bis(diphenylphosphine)aminopropyltriethoxysilane is synthesized and studied by IR and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies for the first time. Chemical modification of silica with (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>N(PPh<sub>2</sub>)<sub>2</sub> gives the support ( $\gamma$ -DPAMPS) containing identical N(PPh<sub>2</sub>)<sub>2</sub> ligands on its surface. Subsequent treatment of the support with (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> and ClPPh<sub>2</sub> gives a silica surface containing two types of attached ligands, NH<sub>2</sub> and N(PPh<sub>2</sub>)<sub>2</sub>, in the ratio ~1:1. The heterogenized complexes Ni-HMC, prepared by ligand exchange between Ni(PPh<sub>3</sub>)<sub>n</sub> (n = 3, 4) and  $\gamma$ -DPAMPS, in combination with Et<sub>2</sub>AlCl exhibit activity and selectivity for ethylene dimerization.

Reaction of Ziegler-Natta catalyst components produces various precursors of active centers that differ in metal valence and bound ligands [1]. This encumbers the study of the olefin oligomerization mechanism in the presence of these catalysts. The situation is very complicated for heterogenized metal complexes (HMC) since active center precursors differing in composition and structure are formed during heterogenization. For example, it was demonstrated in [2] that Ni-HMC synthesized by ligand exchange of Ni(CO)<sub>4</sub> and PPh<sub>3</sub> in the adsorption layer of the support gives at least three types of attached complexes with different ligands.

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Fig. 1. Diffuse reflectance IR spectra of phosphinated silica S-120: a) starting silica calcined at 600°C; b)  $\gamma$ -AMPS; c)  $\gamma$ -AMPS after treatment with Ph<sub>2</sub>PCl; d)  $\gamma$ -DPAMPS.

Fig. 2. Ligand exchange between  $\gamma$ -DPAMPS and Ni(PPh<sub>3</sub>)<sub>n</sub>.

Obviously, it is very important to form active center precursors of identical composition and structure. This can be accomplished most reliably using chemically modified supports. Use of such supports can produce catalysts for different reactions [3]. In particular, immobilization of Rh and Pd complexes on silica gels modified with Schiff bases or aminophosphine groups gives HMC that are active in olefin hydrogenation and isomerization [4].

In the present work, Ni-HMC are synthesized on silica gel modified with aminophosphine ligands and the stepwise formation of ligands and the catalytic activity of the Ni-HMC-Et<sub>2</sub>Al-Cl system for ethylene dimerization are studied.

### EXPERIMENTAL

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker WM-250 and AM-300 spectrometers at 22°C in  $C_6D_6$  or CDCl<sub>3</sub>. The chemical shifts (CS) (±0.03 ppm) of H and C atoms are given relative to TMS. Spin-spin coupling constants  $J^{13}C-H$  were found with an accuracy of ±0.09 Hz. The <sup>31</sup>P CS were determined relative to an internal standard of 85% H<sub>3</sub>PO<sub>4</sub>.

IR transmission spectra between 500-3500 cm<sup>-1</sup> and diffuse reflectance spectra between 2500-3500 cm<sup>-1</sup> were taken from a Hitachi M-340 spectrometer at 20°C. GLC analysis was performed as in [2].

The following reagents were used. Ethylene TU-38 102282-75, industrial PPh<sub>3</sub> recrystallized from alcohol, silica silochrom S-120 ( $S_{sp} = 120 \text{ m}^2/\text{g}$ , pore diameter 40-50 nm, pore volume 1.22-1.44 cm<sup>3</sup>/g), and vacuum-distilled  $\gamma$ -aminopropyltriethoxysilane AGM-9.

All syntheses of metal complexes, supports, and phosphorus-containing compounds and operations with catalyst were carried out under an Ar atmosphere using absolute solvents distilled under Ar.

Dichlorophosphine was prepared by refluxing  $PCl_3$ ,  $C_6H_6$ , and  $AlCl_3$  with subsequent treatment with  $POCl_3$ , as in [5]. Chlorodiphenylphosphine was synthesized from dichlorophenylphosphine and  $AlCl_3$  according to [3]. Physicochemical properties and <sup>31</sup>P NMR spectra of the product were in complete agreement with [6, 7].

 $\gamma$ -Aminopropyl-containing silochrom ( $\gamma$ -AMPS) was prepared by the following method. A 0.8 mole portion of  $(EtO)_3Si(CH_2)_3NH_2(A)$  in 20 ml  $C_6H_6$  was added dropwise to a boiling mixture of 20 g silochrom that was previously calcined in vacuum (600°C, 10<sup>-4</sup> torr, 6-8 h) and 180 ml  $C_6H_6$ . The mixture was stirred for 3 h. The silica was separated, washed with  $C_6H_6$ , and dried in vacuum (10<sup>-4</sup> torr, 6 h, 100°C). The NH<sub>2</sub> content determined by titration according to [3] was 0.173 mmole/g.

The phosphine groups were attached to silochrom by reaction of  $Ph_2PC1$  with  $\gamma$ -AMPS. A calculated volume of a 20% solution of  $Ph_2PC1$  in  $C_6H_6$  was added to a portion of  $\gamma$ -AMPS in  $C_6H_6$  (10 ml per 1 g) and Et<sub>3</sub>N (a quantity equimolar with  $Ph_2PC1$ ) at 60°C over 4-6 h. The IR spectra of the starting S-120,  $\gamma$ -AMPS and its phosphinated form are given in Fig. 1.

Phosphinated  $\gamma$ -aminopropyltriethoxysilane (IV) was prepared the same as the phosphinated  $\gamma$ -AMPS. A 17.2 mmole portion of Ph<sub>2</sub>PCl in 20 ml C<sub>6</sub>H<sub>6</sub> was added dropwise with stirring to a mixture of 8.6 mmoles (A) and 17.2 mmoles Et<sub>3</sub>N in 50 ml C<sub>6</sub>H<sub>6</sub> at 8-10°C. Stirring was continued for 40-50 min at 20°C. The precipitate of Et<sub>3</sub>N·HCl was filtered off. The filtrate was heated 4-6 h at60°C in vacuum (10<sup>-2</sup> torr) after removal of solvent. Found, %: C, 67.28; H, 6.87; N, 2.20; P, 10.23. (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>N(PPh<sub>2</sub>)<sub>2</sub>. Calculated, %: C, 67.23; H, 6.96; N, 2.38; P, 10.53%.

NMR spectrum of (IV) ( $\delta$ , ppm): 1.09 t (9H, CH<sub>3</sub>), 3.60 q (6H, CH<sub>2</sub>O), 0.18 t (2H, CH<sub>2</sub>·Si $\equiv$ ), 3.22 quint (2H, CH<sub>2</sub>), 1.22 t (2H, NH), 7.20-7.83 m (30H, Ph). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 18.52 (CH<sub>3</sub>), 58.30 (CH<sub>2</sub>O), 8.25 (CH<sub>2</sub>Si), 25.33 (CH<sub>2</sub>), 56.45 t (CH<sub>2</sub>N $\equiv$ ), 127.64-140.78 (Ph).

According to elemental analysis, the phosphination product (A) is (IV). The mixture of triphenylphosphine complexes Ni(PPh<sub>3</sub>)<sub>n</sub> (n = 3, 4) was synthesized according to [8].

The Ni-HMC were synthesized by ligand exchange. A portion of  $\gamma$ -AMPS and an equimolar (calculated for the support PPh<sub>2</sub> groups) amount of Ni(PPh<sub>3</sub>)<sub>n</sub> in C<sub>6</sub>H<sub>6</sub> (10 ml per 1 g support) were stirred for 4-6 h. The Ni-HMC was separated, washed with C<sub>6</sub>H<sub>6</sub>, and dried in vacuum (20°C, 10<sup>-2</sup> torr, 4-6 h). The Ni content according to atomic absorption spectroscopy was 0.33-0.34%.

Ethylene dimerization was carried out as described in [9] by successively adding under an Ar atmosphere catalyst, 100 ml  $C_6H_6$ , ethylene, and a solution of  $Et_2AlCl$ .

## RESULTS AND DISCUSSION

The attachment of  $PPh_2$  groups to the surface occurs in two steps using the reagents described in [4] for the synthesis of Rh-HMC

$$\begin{array}{c} = -\text{OH} + (\text{EtO})_{3}\text{Si}(\text{CH}_{2})_{3}\text{NH}_{2} \rightarrow \begin{array}{c} = -\text{O}-\begin{array}{c} \text{Si}(\text{CH}_{2})_{3}\text{NH}_{2} & (1) \\ & (1) \\ & (1) \end{array}$$

$$(1) + 2\text{CIPPh}_{2} \rightarrow \begin{array}{c} = -\text{O}-\begin{array}{c} \text{Si}(\text{CH}_{2})_{3}\text{N}-\text{PPh}_{2} \\ & H \end{array} \\ & (1) \end{array}$$

$$\begin{array}{c} (1) \\ & H \end{array}$$

$$\begin{array}{c} (1) \\ & H \end{array}$$

$$(2) \\ & H \end{array}$$

$$\begin{array}{c} (1) \\ & H \end{array} \\ & (1) \end{array}$$

Two silica samples were used as support. The first was heated at 200°C ( $10^{-2}$  torr, 6 h), the second at 600°C ( $10^{-4}$  torr, 6 h).

The conjugation density of NH<sub>2</sub> groups was 0.292 (~1.4 groups/nm<sup>2</sup>) and 0.173 mmole/g (~0.9 groups/nm<sup>2</sup>) for the two samples, respectively. However, the absorption bands (a.b.) of the NH<sub>2</sub> group could not be observed against the background of the hydrogen-bonded OH groups of the support in the IR transimission or diffuse reflectance spectra of the first sample (200°C).\* Characteristic stretching vibrations of the NH<sub>2</sub> group were found in the diffuse reflectance spectra of the second sample at 3375 and 3310 cm<sup>-1</sup> (Fig. 1b). The IR spectroscopic data are consistent with the titration results and indicate attachment of the amino group to the silica surface.

Treatment of the  $\gamma\text{-}AMPS$  sample obtained with  $\text{ClPPh}_2$  showed that the reaction was incomplete.

<sup>\*</sup>The authors thank L. M. Kustov for help with recording and interpreting the diffuse reflectance IR spectra.

The  $\gamma$ -AMPS was phosphinated at a N/P ratio of 1:1 or 1:2. This ratio in the  $\gamma$ -AMPS phosphination product was 1:0.58 or 1:1.01, respectively. Phosphinated silica samples with a N/P ratio of 1:2 could not be prepared.

The principal changes in the IR spectrum of phosphinated  $\gamma$ -AMPS were seen in the C-H region (Fig. 1c). Two a.b. in the 3000 cm<sup>-1</sup> region (3055 and 3010 cm<sup>-1</sup>), as well as a shoulder at 2965 cm<sup>-1</sup> appear. These are characteristic of PPh<sub>3</sub> [10]. The intensity of the amino group a.b. decreased simultaneously.

However, the IR data do not reveal the extent of the phosphination in formation of product (II) or (III).

In order to answer this question, (A) was phosphinated. Isolation and identification of the phosphination products of (A) could indicate the extent of reaction (2). Since the reaction conditions were identical, phosphination of model compound (A) and (I) can be considered to occur identically. The elemental analyses show a selective reaction with formation of practically only (IV).

The spectral properties of the compound obtained agree satisfactorily with such a conclusion. The similarity of the IR spectra of (IV) and its analog attest to this. (IV) ( $\nu$ , cm<sup>-1</sup>): 3063, 2987, 2932, 2890, 1488, 1440, 1380, 1200, 1170, 1100, 980, 940, 850, 675, 525; CH<sub>3</sub>N(PPh<sub>2</sub>)<sub>2</sub> [11]: 3070, 2995, 2930, 1478, 1430, 1173, 1093, 631, 522. IR spectra of (IV) do not contain a.b. at 3300-3370 and 1600-1630 cm<sup>-1</sup>, as well as a.b. at 1540 cm<sup>-1</sup> that are characteristic of NH<sub>2</sub> and NH groups, respectively [12-14]. Moreover, a.b. occur at 1440 cm<sup>-1</sup> (vibrations of Ph rings bonded to P atoms) and 3000 cm<sup>-1</sup> (CH in Ph).

The <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra confirm the structure of (IV). They agree well with spectra of the corresponding analogs [15, 16]. Data for the <sup>31</sup>P{<sup>1</sup>H} spectra are given below for a number of compounds  $(\delta, \text{ppm})$ : (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>N(PPh<sub>2</sub>)<sub>2</sub>, 63.11; EtN(PPh<sub>2</sub>)<sub>2</sub> [14], 61.80; EtNHPPh<sub>2</sub> [14], 40.04. Thus, (IV) does not contain NHPPh<sub>2</sub> fragments (~40 ppm) but only N(PPh<sub>2</sub>)<sub>2</sub> groups (63.11 ppm).

It is interesting that the <sup>13</sup>C CS of the  $CH_2$  groups (56.45 ppm) after phosphination approaches that of the C atoms in the  $CH_2O$  group (58.30 ppm). The splitting of the signal of this group by P atoms (triplet with coupling constant 11.0 ± 0.6 Hz) confirms the proposed structure of (IV).

Thus, reaction of  $ClPPh_2$  with  $NH_2$  groups of (A) does not present noticeable steric hindrances. Both H atoms are replaced by amino groups to form (IV).

Data for the action of oxygen on (IV) are important regarding use of it as an isolated ligand or one attached to a support. Separate experiments found that (IV) is apparently oxidized on contact with air (20°C). Judging from the  ${}^{31}P{}^{1}H$  NMR data, the content of (IV) in a sample contacted with air becomes  $\leq 15\%$  (~63 ppm). Strong signals at 38-42 ppm appear.

In order to prepare a chemically modified support containing ligands of identical composition, we attempted to attach (IV) to a silochrom surface.

$$= -OH + (EtO)_3Si(CH_2)_3 - N(PPh_2)_2 \rightarrow = -O-Si-(CH_2)_3N$$
(3)

T 1 T 1

The aminobis(diphenylphosphine) groups were fixed to the support surface on treatment of silica with a benzene solution of (IV). This was confirmed by diffuse reflectance IR spectra (Fig. 1d). Absorption bands appear at 2850-2920 and 2860-3055 cm<sup>-1</sup> (stretches of CH bonds in CH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub> groups, respectively). Comparison of Figs. 1c and d shows that the silochrom sample that is modified chemically according to Eqs. (1) and (2) contains a.b. of CH<sub>2</sub> groups along with the above. The analytical and spectral data for stepwise phosphination of silochrom suggest that about half of the amino groups bound to the support are unavailable for Ph<sub>2</sub>PC1.

The Ni-HMC was synthesized by ligand exchange, similar to that described for Rh-HMC[3]. Ni-HMC were not obtained earlier by a similar method. The reaction was carried out according to (4)

$$(III) + \text{Ni}(\text{PPh}_3)_n \to \begin{bmatrix} -0 & -S_1 \\ -S_2 & -S_1 \\ -S_2 & -N(\text{PPh}_2)_2 \text{Ni}(\text{PPh}_3)_{4-m} \\ n = 3, 4 & m = 2, 3 \end{bmatrix}$$
(4)

Treatment of phosphinated  $\gamma$ -AMPS (III) with a benzene solution of Ni(PPh<sub>3</sub>) gives Ni-HMC(V). The kinetics of ligand exchange were followed in a series of parallel experiments with identical amounts of (III) and correspondingly equal volumes of Ni(PPh<sub>3</sub>)<sub>n</sub> solutions of the same concentration. The Ni content in (V) was found by atomic absorption spectroscopy. The highest Ni content in (V) was attained after 4 h (Fig. 2).

The catalytic properties of Ni-HMC (V) for ethylene dimerization were studied using Et<sub>2</sub>AlCl as activator. The activity of Ni-HMC-Et<sub>2</sub>AlCl under the conditions chosen ( $C_6H_6$ , 50°C,  $PC_2H_4 = 0.1$  MPa, [Al]/[Ni] = 50) was 1800 mole  $C_2H_4/g$  atom Ni·min. The selectivity for  $\Sigma C_4 = 94.7\%$  (remaining products were 5.2% hexenes and 0.1%  $\Sigma C_{g+}$ ). The (V) prepared is similar in effectiveness to more active Ni-HMC samples that have been described [9].

Thus, Ni-HMC were synthesized based on phosphinated  $\gamma$ -AMPS which in combination with Et<sub>2</sub>AlCl exhibit high activity and selectivity in ethylene dimerization.

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