Binuclear nickel–ylide complexes as effective ethylene oligomerization/polymerization catalysts

Atanas Tomov, Kurti Kurtev *

Higher Institute of Chemical Technology, Department of Basic Organic Synthesis, 8010 Bourgas, Bulgaria

Abstract

Binuclear nickel–ylide complexes based upon different bis-α-ketoylides were studied as catalysts in ethylene oligomerization/polymerization. The products of oligomerization reactions are mixtures of C_4–C_{20} olefins, whose molecular weight distributions do not comply with the Schultz–Flory type. Their linearity and α-portion are lower than those obtained by the corresponding mononuclear catalysts. The binuclear nickel–ylide complexes are more active ethylene polymerization catalysts compared to the corresponding mononuclear ones. The higher activity of the binuclear nickel–ylide complexes was discussed on the basis the influence of the moiety linking the active centers (electronic and steric properties of the linking groups) and the distance between them.

Keywords: Binuclear complexes; Ethylene; Nickel; Oligomerization; Polymerization; Ylide complexes

1. Introduction

Nickel–ylide complexes of the type [NiPh{Ph$_2$PCR^1=C(O)R^2}L] (L = phosphine), are well known as effective catalytic precursors for ethylene oligomerization to linear α-olefins [1–14]. A complex of that kind, [NiPh{Ph$_2$PCH=C(O)Ph}(PPh$_3$)] models the large-scale industrial process for the production of linear α-olefins by giving high yields and excellent selectivities (99$^+$%) when used as a catalyst for the oligomerization of ethylene [15]. It has been shown by Klabunde and co-authors that such organotransition metal compounds can be easily converted into ethylene polymerization/copolimerization catalysts, using phosphine scavengers

[16–19]. The role of the phosphine scavengers has been attributed to scavenging the phosphine ligands from the solution, thus converting the ethylene oligomerization nickel–ylide catalyst into polymerization one, although some nickel–ylides are known as effective polymerization catalysts even without presence of scavengers in the catalytic solution [20–25].

Concerning the catalytic activity of the nickel–ylide complexes in ethylene oligomerization/polymerization, it has been found that it strongly depended upon the ligand moiety. Especially for the mononuclear catalysts it has been shown that the presence of some electron-withdrawing groups in the chelate rings of the complexes can have a positive effect on their catalytic activity [26]. However these data have mainly empirical

---

* Corresponding author. Phone (+359-56)660017; Fax: (+359-56)686141

character and cannot be used for prediction of the activity of the catalysts.

Only Peuckert, Keim and Weber, have reported a linear relationship between the electron density of the nickel co-ordination centre and the activation enthalpy of the oligomerization reaction carried out in presence of mononuclear nickel–ylide and acetylacetonate complexes [27].

Although a large variety of complexes have been synthesized and studied as ethylene oligomerization/polymerization catalysts, the data concerning the use of binuclear nickel–ylide complexes such as ethylene oligomerization/polymerization catalysts are very scarce [28].

Recently we have established that the binuclear nickel–ylide complexes, based on bis-α-ketoylides [29], are more active ethylene polymerization catalysts than the corresponding mononuclear ones, when applied with phosphine scavengers [30]. It was assumed that the higher activity of the binuclear complexes is due to the mutual electronic interactions of the active centers, especially when they take part in a conjugated system. It was also found that the catalytic activity of these complexes increased when bulky substituents are involved in their chelate rings.

Most of the binuclear nickel–ylides are also active ethylene oligomerization catalysts, when used without adding phosphine scavengers, but the product linearity is lower than that observed by the corresponding mononuclear catalysts.

In the present paper we attempt to gain better insight into the catalytic properties of the binuclear nickel–ylide complexes in ethylene oligomerization/polymerization and their catalytic activity. It was found that the binuclear nickel–ylide activity well correlates to the difference of the force constants of keto- and ylide groups in the bis-α-ketoylides before and after their co-ordination to the nickel atoms. This paper deals with the influence of changes in the type and the length of the organic groups linking the active centers, and the substituents of the chelate parts on the catalytic behaviour of the binuclear nickel–ylides in ethylene oligomerization/polymerization.
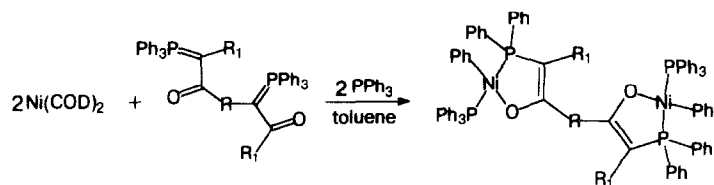
2. Experimental

All reactions were carried out under dry argon, using standard Schlenk techniques. Bis-α-ketoylides were synthesised according to [29]. The binuclear nickel–ylide complexes (Scheme 1) were synthesised and analyzed as described in [30]. Oligomers were analysed by capillary GC on a Perkin Elmer Sigma 2000 chromatograph, equipped with a flame-ionization detector. Data handling was provided by the Chromatographics 2 Data System (Perkin Elmer). Permaphase DMS (dimethylsylicone) fused-silica capillary columns (50m × 0.25 mm i.d.; two columns in series connected with butt connector) used in our work were from Perkin Elmer. Polymer characterisation was performed using FT-IR, DSC (Stream DSC-111), GPC (ALC/GPC-150C, Waters).

2.1. General procedure for ethylene oligomerization/polymerization by the binuclear nickel–ylide complexes

Ethylene oligomerizations/polymerizations were carried out as described in [30]. The reactions, typically run for 1–6 h and after subsequent cooling, were terminated by release of the ethylene pressure. In the case of oligomerization, liquid samples for GC analysis were withdrawn every 30 min via a three-way stop cock using a suitably precooled syringe. In the case of ethylene polymerization, the reactor contents were transferred to a beaker containing methanol (300 ml). The resulting polymer residues were washed with methanol while white polyethylene samples were obtained.

3. Results and discussion

It is well known that the nickel OP chelate complexes are active catalysts for ethylene oligomerization to higher α-olefins [5]. They can be readily converted into ethylene polymerization catalysts by applying phosphine scavengers [16].

Catalyst Nᵒ	R	R₁	Yield, %
1	1,4-C₆H₄	H	50
2	1,3-C₆H₄	Ph	54
3	-(CH₂)₈-	Ph	70
4	-(CH₂)₈-	CO₂Me	52
5	-(CH₂)₄-	CO₂Me	51
6		Ph	72
7	1,1'-(η⁵-C₅H₄)₂Fe	Ph	69
8	1,1'-(η⁵-C₅H₄)₂Fe	Me	64
9	1,4-C₆H₄	SO₃Na	65

Scheme 1. Synthesis of binuclear nickel–ylide complexes.

The binuclear nickel–ylide complexes are also able to oligomerize or polymerize ethylene depending on the reaction conditions. Although these binuclear species contain the same type of catalytic active centers as the mononuclear ones, their catalytic properties (activity, product distribution, lifetime) are different. They mainly depend on the organic group linking the chelate parts, the substituents into the chelate rings, the distance between them, the presence of conjugation between the active centers, etc.

Some of the binuclear nickel–ylides, for example 3, 5 and 6, oligomerize ethylene but the product linearity is lower than those obtained by the related mononuclear complexes. Complexes 1, 2 and 9 polymerize ethylene even without phos-

phine scavengers thus producing low molecular weight polyethylene. Complexes 7 and 8 are catalyticaly inactive without applying phosphine scavengers. All the binuclear nickel–ylide complexes (1–9) polymerize ethylene in presence of phosphine scavengers to give polyethylene.

3.1. Ethylene oligomerization

Complexes 3, 5 and 6 at temperatures from 333 to 358 K, in toluene solution, oligomerize ethylene to give higher olefin mixtures. Data concerning the catalytic activity and the oligomer distribution are listed in Table 1 and Table 2. As it is shown in Table 1 the catalyst activities depend on the catalyst concentration, ethylene pressure, catalyst

Table 1
Activities of binuclear nickel–ylide catalysts 3, 5 and 6 for ethylene oligomerization in toluene at 343 K

Run no.	Catalyst no.	$C_{catalyst}$ mmol/l	$P_{ethylene}$ MPa	Activity g ethylene/g Ni·h
1	5	5.00	1.0	470
2	5	2.88	1.0	590
3	5	2.77	1.8	700
4	5	2.77	0.6	320
5	5	1.72	1.0	760
6	5	1.00	2.3	1400
7	3	5.00	1.0	340
8	3	2.77	1.0	440
9	3	3.50	1.7	430
10	3	1.70	2.3	830
11	3	1.70	1.7	590
12	3	1.00	2.3	1020
13	6	5.00	2.2	760
14	6	5.00	1.6	450
15	6	5.00	1.0	260
16	6	2.50	2.2	1100
17	6	2.50	1.6	810
18	6	2.50	1.0	530
19	6	1.00	2.3	1450

Table 2
Molecular weight distribution of oligomers obtained by binuclear nickel–ylide catalysts 3, 5 and 6 (GC data)

Catalyst no.	Oligomer distribution [a] (%)								
	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}
3	4.0	12.0	21.7	18.0	18.0	15.9	10.0	0.5	0.1
5	5.3	20.6	26.4	18.4	11.1	9.1	7.1	1.7	0.3
6	5.5	8.4	24.5	20.1	17.7	17.4	6.0	traces	traces

Reaction conditions: $P_{ethylene} = 2.3$ MPa; $C_{catalyst} = 1.00$ mmol/l; $T = 343$ K; solvent = toluene.
[a] $C_{catalyst} = 1.00$ mmol/l; $P_{ethylene} = 2.3$ MPa.

structure. The increase of the ethylene pressure (runs 3, 4; 10, 11; 16, 17 and 18) as well as the decrease of the catalyst concentration (runs 1, 2; 7, 8, 9 and 11; 15 and 18) leads to an increase of the catalytic activity. It can be stated that the most active ethylene oligomerization catalyst is 6 (compared to 3 and 5). No substantial explanation for its higher activity was derived, but probably the close distance between the chelate parts, as well as the bulkiness of the norbornene ring play a role. In the case of complex 5 it was clear that its higher activity compared with 3 is due to the

presence of stronger electron-withdrawing groups (CO_2CH_3) along with the closer distance between the active centers.

The molecular weight distribution of the oligomers obtained by the binuclear nickel–ylide catalysts is shown in Table 2 and Fig. 1. In general, three types of distributions are possible: 1) unimodal distribution – in the cases of uniformity of the catalytic centers; 2) bimodal distribution – in the cases of difference of the active centers, their activity and tendencies toward β-hydride elimination; 3) asymmetric distribution curves, owing to two or more unresolved peaks – in the cases of slim different active centers; or identical active centers, located in different stereochemical environments, which makes their activities and β-hydride elimination rates slight different. This case can also occur when the catalyst molecule exists as more than one diastereomer or conformational isomers taking part in a catalytic reaction.

The asymmetric appearance of the distribution curves shown on Fig. 1 can be attributed to the existence of the catalyst molecules in one or more preferable conformers in which the active centers are located in different stereochemical environments, as they are chemically and structurally equal. It can also be used as evidence for the simultaneous action of both the active centers.
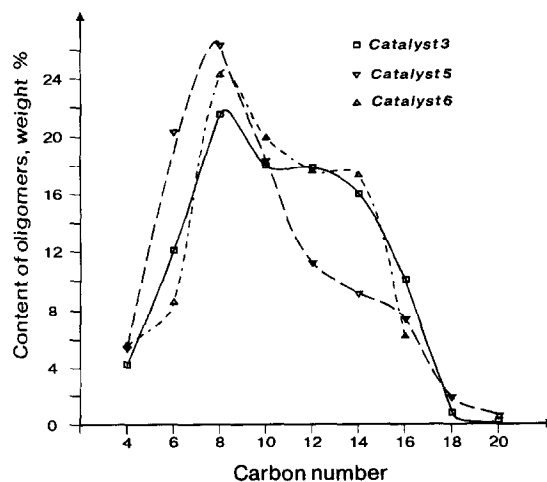

Fig. 1. Molecular weight distributions of oligomers obtained by binuclear nickel–ylide catalysts 3, 5 and 6 (GC data); Reaction conditions: $P_{ethylene} = 2.3$ MPa; $C_{catalyst} = 1.00$ mmol/l; $T = 343$ K; solvent = toluene.

Table 3

Product distribution (GC determined) of $C_6^=$ fraction obtained by binuclear nickel–ylide catalysts 3, 5 and 6

C_6 alkene [a]	Catalyst		
	3	5	6
3-methyl-1-pentene	1.0	0.0	0.9
1-hexene	70.1	42.6	60.2
2-ethyl-1-butene	9.2	29.0	11.2
trans-3-hexene	1.8	5.2	11.3
cis-3-hexene	0.4	1.0	0.7
trans-2-hexene	7.9	15.0	6.3
cis-3-methyl-2-pentene	3.4	0.1	1.1
cis-2-hexene	5.2	7.0	8.2
trans-3-methyl-2-pentene	0.3	0.1	0.1
unidentified	0.7	0.0	0.0
linearity, %	85.4	70.8	86.7
α-portion, %	80.3	71.6	72.3

Reaction conditions: $P_{ethylene} = 2.3$ MPa; $C_{catalyst} = 1.00$ mmol/l; $T = 343$ K; solvent = toluene.
[a] $C_{catalyst} = 1.00$ mmol/l; $P_{ethylene} = 2.3$ MPa.

The data concerning the product distributions of the 'hexene' fraction, obtained from ethylene oligomerization with complexes 3, 5 and 6 are presented in Table 3. The presence of 2-ethyl-1-butene indicates that the binuclear nickel–ylide catalysts are able to co-oligomerize ethylene with 1-butene formed in situ (Scheme 2). We also assume that the mechanism of co-oligomerization could include stages of intramolecular substrate transfer, in which both the active centers take part. In this context comparison of the product distribution obtained by 3, 5 and 6 to that reported by Keim and Behr for mononuclear nickel–ylides [13] shows that the mononuclear complexes are able to produce only linear (99^+) α-olefins when starting from pure ethylene. In the presence of α-olefins however, these complexes cooligomerize ethylene to give branched products [11].

The highest 2-ethyl-1-butene content in C_6 fraction obtained by catalyst 5 indicates that this complex possesses strongest co-oligomerization ability (due to the close disposition of its active centers – 4 methylene groups). In contrast, the 2-ethyl-1-butene content in oligomers obtained by

catalyst 3 is lowest, which can be attributed to the relative remoteness of its active centers (8 methylene groups). Although the active centers of catalyst 6 are closest in distance, their trans-configuration decreases the in situ co-oligomerization ability of this complex. Thus the 2-ethyl-1-butene content in the C_6 fraction obtained by 6 is close to that typical for complex 3.

On the other hand, as can be seen from Table 3, the lowest linearity and α-portion of the hexenes are characteristic for catalyst 5, in which the active centers are at close distance. The trans-position of the chelate parts in 6 makes them interact not as strongly as in 5, independently of their close disposition, which is confirmed by the linearity and α-portion of the corresponding C_6 fraction.

Similar conclusions may be drawn for the 'octene' fraction. For example the 2-ethyl-1-hexene (co-polymerization product) content in C_8 fraction obtained by catalyst 3 is 2.80%, while in the cases with catalysts 5 and 6 it is 5.53 and 3.45%, respectively.

Taking into account the above mentioned it may be summarised that the closer the distance between the active centers the stronger the interaction between them, and the longer distance between the active centers the closer the behaviour of the binuclear nickel–ylides to that of the mononuclear ones.

3.2. Ethylene polymerization

The binuclear nickel–ylide complexes, in the presence of phosphine scavengers polymerize ethylene to give polyethylene. No oligomers were obtained under these conditions. The results from a variety of polymerization runs are listed in Table 4. As effective phosphine scavengers were used $Ni(COD)_2$, $Rh_2(C_2H_4)_4$-μ-Cl_2, $Rh_2(COD)_2$-μ-Cl_2 and $PdCl_2(CH_3CN)_2$ (COD-cis, cis-1,5-cyclooctadiene). In preliminary experiments it was found that the phosphine scavengers used are not able to oligomerize/polymerize ethylene without the presence of a nickel–ylide complex.
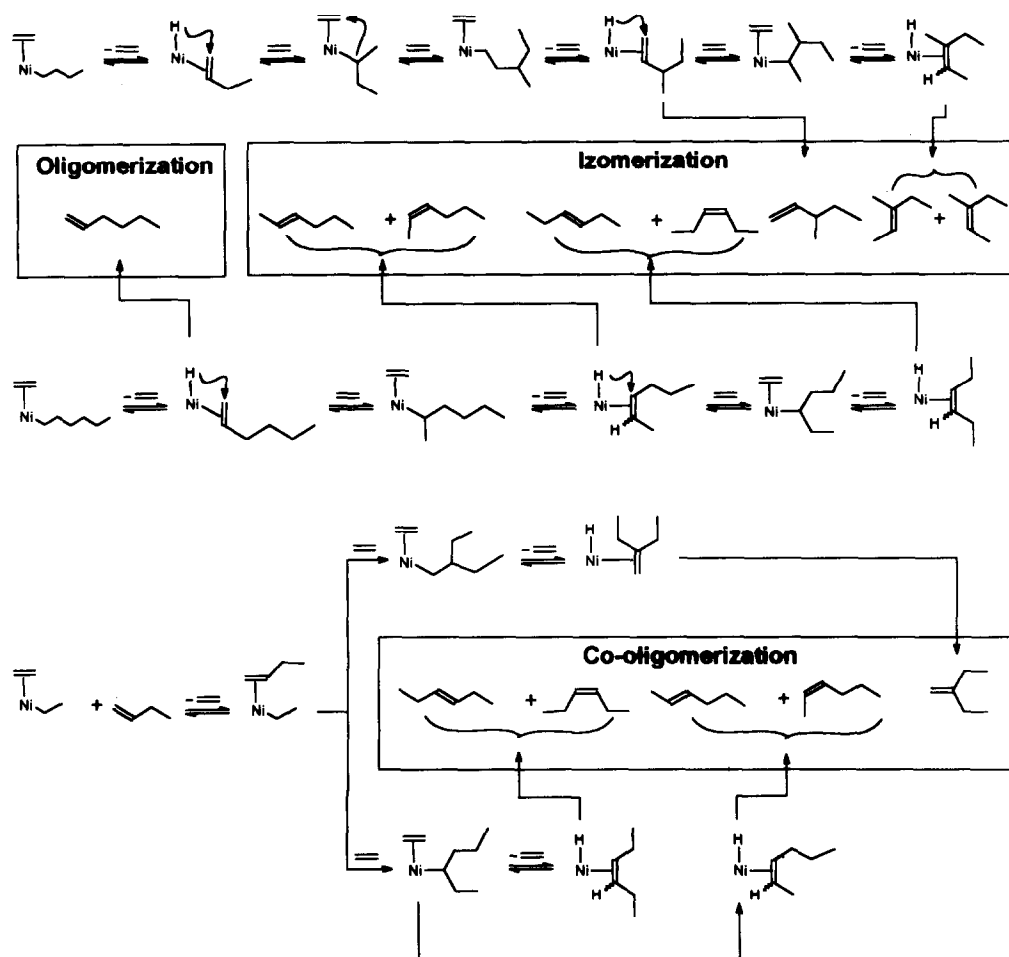
Scheme 2. Supposed mechanism for obtaining isomeric hexenes in the ethylene polymerization by the binuclear nickel–ylide catalysts.

Table 4
Ethylene polymerization by catalytic systems binuclear nickel–ylide catalyst/phosphine scavenger

Run no.	Catalyst no.	Phosphine scavenger [a]	Solvent	$C_{catalyst}$ mmol/l	$C_{scavenger}$ mmol/l	$P_{ethylene}$ MPa	T K	Activity [b] kg PE/g Ni·h
1	1	Ni	toluene	0.42	1.60	0.8	323	3.20
2	1	Ni	toluene	0.42	1.60	1.6	324	4.30
3	1	Ni	toluene	0.42	1.62	2.0	324	5.0
4	1	Ni	toluene	0.42	1.60	2.5	325	5.65
5	1	Ni	toluene	0.83	3.18	0.8	325	0.55
6	1	Ni	toluene	0.72	2.81	0.8	324	0.85
7	1	Ni	toluene	0.55	2.02	0.8	323	2.00
8	1	Ni	heptane	0.42	1.66	1.6	323	3.20
9	5	Ni	THF	0.28	0.87	2.5	324	4.22
10	6	Ni	acetone	0.43	1.62	1.7	324	6.15
11	5	Rh-1	methanol	0.33	0.35	2.6	324	0.32
12	6	Ni	methanol [c]	0.16	1.12	1.7	323	1.48

[a] Ni is Ni(COD)$_2$; Rh-1 is Rh$_2$-μ-Cl$_2$(C$_2$H$_4$)$_4$.
[b] Includes only Ni from catalyst, not from phosphine scavenger
[c] 88% solution of methanol in water.

Table 5
Force constants f (FT-IR determined) of the C=O and C=P bonds in the binuclear nickel–ylide complexes and the corresponding bis-α-ketoylides

Catalyst no.	$f_{C=O,complex} \times 10^{-5}$ dyn/cm	$f_{C=O,ylide} \times 10^{-5}$ dyn/cm	$\Delta f_{C=O}$ [a] $\times 10^{-5}$ dyn/cm	$f_{C=P,complex} \times 10^{-5}$ dyn/cm	$f_{C=P, ylide} \times 10^{-5}$ dyn/cm	$\Delta f_{C=P}$ [b] $\times 10^{-5}$ dyn/cm	Activity [c] kg PE/g Ni·h
1	9.38	9.44	−0.06	9.62	9.66	−0.04	2.80
2	9.82	9.90	−0.08	8.41	8.57	−0.16	2.18
3	9.73	9.82	−0.09	8.21	8.51	−0.30	0.52
4	9.29	9.54	−0.25	9.10	9.70	−0.60	0.23
5	8.82	8.92	−0.10	9.14	9.41	−0.27	1.03
6	8.98	8.88	0.10	9.71	9.50	0.21	8.15
7	8.83	9.00	−0.17	8.57	9.71	−1.14	0.06
8	8.82	9.95	−0.13	8.51	9.77	−1.26	0.03
1′ [d]	9.17	9.36	−0.19	9.17	9.80	−0.63	0.23 [e]

[a] $\Delta f_{C=O} = f_{C=O, complex} - f_{C=O, ylide}$.
[b] $\Delta f_{C=P} = f_{C=P, complex} - f_{C=P, ylide}$.
[c] Reaction conditions: $P_{ethylene} = 0.5$ MPa; $C_{catalyst} =$ the lowest effective catalyst's concentration; $T = 323$ K; solvent = toluene.
[d] Data about the IR spectra – as reported by Kowaldt [31].
[e] Data as reported by Klabunde et al. [16].

The binuclear nickel–ylides, similarly to the corresponding mononuclear ones [8] are catalytic precursors which are able to generate catalytic active 'nickel–hydrides' at higher temperature in the presence of substrate molecules. For example the activation temperature for complex 6 in the liquid phase ethylene polymerization was 45°C, while for complexes 7 and 8 heating the reaction mixture to 65°C was required.

A number of polymerization reactions, in the presence of binuclear nickel–ylide complexes, were carried out at different ethylene pressures and catalytic concentrations to find out the influence of these process parameters on the catalyst activity. Thus the increase of the ethylene pressure (Runs 1–4), as well as the decrease of the catalyst concentration (Runs 5–7) led to a significant increase of catalyst activity.

The ethylene polymerizations were usually carried out in toluene, although heptane, acetone and tetrahydrofuran are also acceptable (Runs 8–10). Some of the binuclear nickel–ylide complexes are able to polymerize ethylene in methanol and even in methanol–water mixtures (Runs 11–14). The activity of the binuclear nickel–ylide depend on the type of solvent used. The most appropriate solvents in the ethylene polymerization, towards the catalytic activity, were found to be the non-polar aprotic solvents such as toluene or heptane. The using of polar solvents as the reaction medium leads to a significant decrease of the activity of the binuclear nickel–ylide catalysts. However some of the catalysts under question, for example 6, possess high resistance with regard to polar solvents (Run 14).

Concerning the activity of the binuclear nickel–ylide catalysts it was found that it correlated well to the difference of the force constants of the ylide as well as the carbonyl groups in the bis-α-ketoylides and the corresponding binuclear complexes (Table 5). The force constants, f were calculated using the following equation:

$$f = 4 \cdot \mu \cdot \nu^2 \cdot \pi^2 \cdot c^2$$

where ν is the stretching vibrations of the corresponding bond, cm^{-1}; $\pi = 3.142$; c is the velocity of the light, cm/s; μ is the reduced mass of the linked atoms A and B, e.g., C=O or C=P, g:

$$\mu = M_A \cdot M_B / (M_A + M_B)$$

The difference of the force constant of the ylide group and the carbonyl group in the bis-α-ketoylides and the corresponding binuclear complexes were calculated using the following equations:
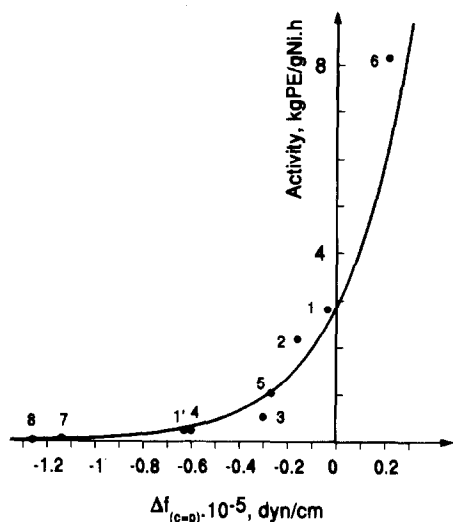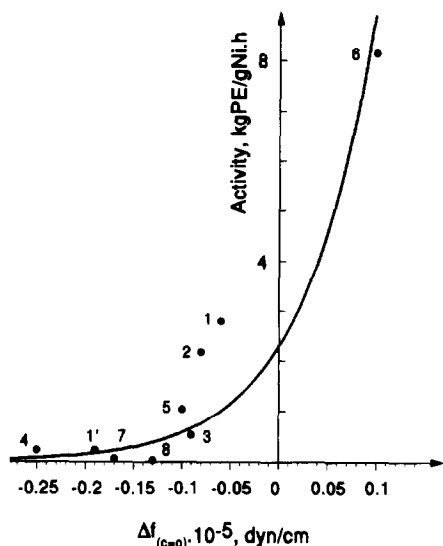
Fig. 2. Correlation plot of the activity of the binuclear nickel–ylide catalysts **1–9**, and the mononuclear complex **1'** (see text), in ethylene polymerization versus $\Delta f_{C=P}$.

Fig. 3. Correlation plot of the activity of the binuclear nickel–ylide catalysts **1–9**, and the mononuclear complex **1'** (see text), in ethylene polymerization versus $\Delta f_{C=O}$.

$$\Delta f_{C=P} = f_{C=P,complex} - f_{C=P,ylide}$$

$$\Delta f_{C=O} = f_{C=O,complex} - f_{C=O,ylide}$$

The correlation relationships displaying the activity of the binuclear nickel–ylide catalysts as function of $\Delta f_{C=P}$, or the $\Delta f_{C=O}$ values are shown in Fig. 2 and Fig. 3. An explanation of the relationship shown in Fig. 2, using the Dewar–Chatt–Duncanson model (Fig. 4) is given below.

The change of the C=P bond force constants in the bis-α-ketoylides after their co-ordination to the nickel atoms mainly depends on the back electron donation Ni→P and the electron donation P→Ni. Thus an increase of the back donation Ni→P will cause a decrease of the C=P bond strength as well as its force constant. Contrariwise, the increase of the electron donation P→Ni will cause an increase of the C=P bond strength. On the other hand the stronger back donation Ni→P, the weaker back donation Ni→ethylene, and the stronger donation ethylene→Ni the stronger ethylene activation. In summary, the difference of the force constants between the bis-α-ketoylides and the corresponding binuclear complexes can be used as a measure for the strength of the co-ordination of ethylene to the nickel atoms, correspondingly for the determination of ethylene activation.

The strength of the donor–acceptor interactions between ylide phosphorus and nickel depend on the electron and steric properties of the substituents in the chelate rings of the complexes. To achieve slight back electron donation Ni→P, or strong co-ordination and activation of ethylene, groups with high steric parameters should be involved to the chelate rings of the complexes. For example complex **6** is more active than **3**. This is apparently due to the stronger steric repulsion between the chelate parts and the norbornene ring,
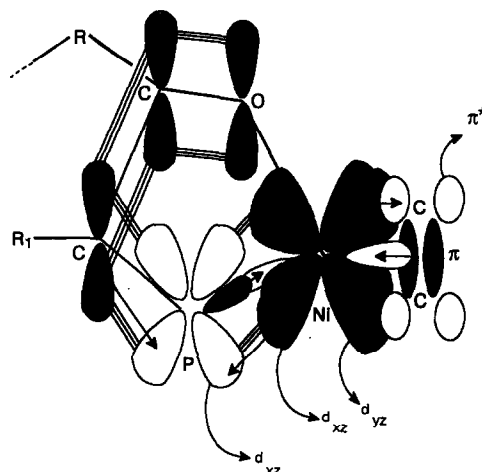

Fig. 4. The Dewar–Chatt–Duncanson model, applied to a binuclear nickel–ylide catalyst in action (the second active center is not shown).

which makes the back donation from Ni to be directed mostly to the co-ordinated ethylene, than to the ylide carbon (Fig. 2 and Fig. 4). The involving of groups which possess $+M$ or $-I$ effect into the chelate rings also positively affect the catalytic activity. For example complex **7** is more active than **8**, which can be attributed to the $-I$, and $+M$ effects of the phenyl substituents linked to the chelate rings of **7**.

Data concerning the catalytic activity of mononuclear analogue of **1**, cited in the literature, [16,31] fit well the correlation relationships shown in Fig. 2 and Fig. 3 (the point marked **1′**). In the case of **1**, in which the chelate rings take part in a conjugated system, the Ni → P back electron donations of the two active centers act oppositely to each other through the conjugated system and mutually decrease themselves (as two opposite directed waves). As a result stronger co-ordination and activation of ethylene occurred, in comparison to **1′**.

Summarised, the higher catalytic activity of the binuclear nickel–ylide complexes, compared to that one of the corresponding mononuclear complexes is due to the close distance interactions of the two active centers. Such interactions cannot be realised either in supported mononuclear complexes, in which the active centers are located farther from each other, or in the solutions of the mononuclear complexes, in which the distances between the molecules of the catalyst are too great.

Acknowledgements

References

[1] W. Keim, Angew. Chem., Int. Ed. Engl., 29 (1990) 235.
[2] W. Keim, Fundam. Res. Homogeneous Catal., 4 (1984) 131.
[3] W. Keim, J. Mol. Catal., 52 (1989) 19.
[4] W. Keim, F. Kowaldt, R. Goddard and C. Krüger, Angew. Chem., 90 (1978) 493.
[5] W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. Kowaldt, U. Kürschner, B. Limbäcker and F. Sistig, Organometallics, 5 (1986) 2356.
[6] W. Keim, New J. Chem., 11 (1987) 531.
[7] Y. Kissin and D. Beach, J. Polym. Sci.: Part A: Polym. Chem., 27 (1989) 147.
[8] W. Keim, Stud. Surf. Sci. Catal., 25 (1986) 201.
[9] G. Nesterov, V. Zakharov, G. Fink and W. Fenze, J. Mol. Catal., 66 (1991) 367.
[10] G. Nesterov, G. Fink and V. Zakharov, Makromol. Chem. Rapid. Commun., 10 (1989) 669.
[11] Y. Kissin, J. Polym. Sci.: Part A: Polym. Chem., 27 (1989) 605.
[12] K. Hirose and W. Keim, J. Mol. Catal., 73 (1992) 271.
[13] A. Behr and W. Keim, Arabian J. Sci. Eng., 10 (1984) 73.
[14] G. Nesterov, V. Zakharov, G. Fink and W. Fenzl, J. Mol. Catal., 69 (1991) 129.
[15] W. Keim, Chem. Ing. Tech., 56 (1984) 850.
[16] U. Klabunde, R. Mülhaupt, T. Herskovitz, A. Janowicz, J. Calabrese and S. Ittel, J. Polym. Sci.: Part A: Polym. Chem., 25 (1987) 1989.
[17] U. Klabunde, US Pat. 4,716,205 (1987).
[18] U. Klabunde and S. Ittel, J. Mol. Catal., 41 (1987) 123.
[19] U. Klabunde, T. Tulip, D. Roe and S. Ittel, J. Organomet. Chem., 334 (1987) 141.
[20] G. Braca, M. Di Girolamo, A.M. Raspolli Galletti, G. Sbrana, M. Brunelli and G. Bertolini, J. Mol. Catal., 74 (1992) 421.
[21] G. Braca, Chim. Oggi., 23 (1988) 11.
[22] K.A. Ostoja Starzewski and J. Witte, Angew. Chem., 97 (1985) 610.
[23] K.A. Ostoja Starzewski and J. Witte, Angew. Chem., 99 (1987) 76.
[24] K.H.A.O. Starzewski, J. Witte and H. Bartl, US Pat. 4,620,021 (28.10.1986).
[25] G. Braca, A. Ricci, G. Sbrana, M. Brunelli, A. Giusti, G. Bertolini and A.M. Raspolli Galletti, E.P. 0 393 751 A2 (1990).
[26] D. Beach and J. Harrison, US Pat. 4,301,318 (17.11.1981).
[27] M. Peuckert, W. Keim, S. Storp and R.S. Weber, J. Mol. Catal., 20 (1983) 115.
[28] D. Matt, M. Huhn, J. Fischer, A. De Cian, W. Kläui, I. Tkatchenko and M. Bonnet, J. Chem. Soc., Dalton Trans., (1993) 1173.
[29] A. Tomov and K. Kurtev, Bulg. Chem. Commun., 25 (1992) 436.
[30] K. Kurtev and A. Tomov, J. Mol. Catal., 88 (1994) 141.
[31] F. Kowaldt, Dissertation, RWTH Aachen, 1977.