Reactions of neutral and ionic square-planar organometallic nickel compounds with ethylene

Rosa Mª Ceder, Josefina Cubillo, Guillermo Muller, Merce Rocamora and Joaquim Sales

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona (Spain)

(Received July 17, 1991)

Abstract

We have studied the reaction of ethylene with a group of $[NiXRL_2]$ complexes with R = 2,4,6-$Me_3C_6H_2$, 3,5-$Cl_2C_6H_3$, 2,3-$Cl_2C_6H_3$, C_6Cl_5, or 2-MeC_6H_4 and L = mainly PPh_3. Migratory insertion and β-elimination of vinyl or butenyl R products was observed, but only under ethylene pressure. The smallest activation energy for this reaction was observed with the complex containing 2,4,6-$Me_3C_6H_2$. Detection of the hydride generated in these reactions has been attempted by formation of a metalacycle using $[NiBr(2,4,6-Me_3C_6H_2)(PPh_2(CH_2CH_2CH=CH_2))_2]$ as the starting complex. The direction of the insertion of propene into the Ni–R bond depends on the size of R. When R = mesityl, 100% of Ni $\rightarrow C_2$ compounds were obtained, whereas for R = 3,5-$Cl_2C_6H_3$, 80% of Ni $\rightarrow C_1$ compounds were recovered.

Many of the hydride species formed in the reactions of neutral and ionic mesityl derivatives $[NiBr(2,4,6-Me_3C_6H_2)L_2]$ and $[Ni(2,4,6-Me_3C_6H_2)(CH_3CN)L_2]BF_4$ (L = PEt_3, PMe_2Ph, PPh_3, $P(^nBu)_3$, $P(^iBu)_3$, PCy_3, PBz_3, dppe or $PN(PPh_2CH_2(2-py))$) with ethylene are able to catalyze the dimerization of ethylene. Bidentate ligands do not show any activity. The insertion of ethylene in the nickel–carbon bonds occurs after prior dissociation of a neutral ligand. The different selectivities are discussed.

Introduction

Nickel(II) complexes are effective catalysts for the oligomerization of olefins [1,2]. A great diversity of products, ranging from dimers to high-molecular-weight polymers, can be obtained using the unusual selectivity-controlling effects of the ligands in homogeneous systems. Dimerization of olefins such as ethylene [3–5], propene [6–8], norbornene [9] and methyl acrylate [10] have been observed with monodentate phosphorus ligands. Oligomers or long-chain polymers of ethylene [11–13] or styrene [14] are obtained with complexes containing bidentate ligands, or with cationic species.

Correspondence to: Dr. M. Rocamora, Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain.

In the absence of experimental evidence of changes in the oxidation state of the metal the Cossee–Arlman mechanism [15] may describe the reaction process. However, in some cases oxidative coupling on Ni^0 species has been proposed [9]. A co-catalyst may be required to scavenge the phosphorus ligand or to activate the complex. It is possible to prepare compounds such as $[Ni(Ph_2PCH=CPhO)Ph]_2$ [16] or $[Ni(mesityl)(CH_3CN)(PBz_3)_2]BF_4$ [17] with at least two coordination positions of the formally tetracoordinated nickel complex available, to be used in the sequence of hydride formation and successive insertion of olefins. These compounds act as a single component catalyst.

Different intermediates related to the active species involved in the various steps of the Cossee mechanism (hydride, olefin–hydride, alkyl and olefin alkyl) have been obtained or detected with different metals. The β-H elimination of an alkyl ligand and the β-migratory insertion of olefins on the M–H or M–alkyl bond are two of the best known reactions in organometallic chemistry. However, in spite of the great amount of information concerning these oligomerizations, the factors controlling the activity and selectivity of the active species towards a given olefin are still very poorly defined.

Complexes $[NiXRL_2]$ (L = phosphine) are also able to dimerize olefins [3,4]. Depending on the ligands and the neutral or ionic nature of the nickel moiety, different behaviours can be observed. In this paper we report our results on several of the reactions involved in the dimerization process of ethylene.

Results and discussion

Migratory insertion of ethylene into the Ni–R bond

Nickel hydride species may be generated from $[NiXRL_2]$ compounds in the presence of ethylene, by insertion of the olefin into the Ni–R bond followed by a β-H elimination from the alkyl intermediate. This reaction must lead to vinyl derivatives of R. When the lifetime of the alkyl intermediate is long enough, a second ethylene insertion becomes possible and 4-butyl species may appear. The results obtained with different $[NiBrRL_2]$ compounds are shown in Table 1. The times and temperatures of reactions were those necessary for total decomposition of the organometallic compound, unless otherwise stated. Steady conditions led to partial decomposition although the distribution of the reaction products did not change. These compounds do not react with ethylene at atmospheric pressure. At room temperature, 30 bar of ethylene is sufficient to allow reaction with the PPh_3 compounds containing o-tolyl, mesityl and 3,5-dichlorophenyl. The compound without an *ortho*-substituted aryl (R = $3,5\text{-}Cl_2C_6H_3$) also produces thermal decomposition products R_2 and BrR. The effects of R and L on the relative stabilities of the organometallic compounds and on the product distribution (vinylR = RC_2 or butenylR = RC_4) seem to be related. The formation of derivatives with RCy is observed only with complexes containing $2,4,6\text{-}Me_3C_6H_2$ or C_6Cl_5, and the biggest phosphines according to Tolman's cone angles. The formation of a butenyl chain (no longer chains were observed) seems to be possible when the steric crowding in the $[Ni\text{-}CH_2\text{-}CH_2\text{-}R]$ complex is large enough to hinder β-H elimination, when a second ethylene insertion becomes competitive. The most crowded complex $[Ni(2,4,6\text{-}Me_3C_6H_2)(C_2Cl_3)(PMe_2Ph)_2]$ gives almost complete double insertion into the mesitylene–nickel bond. Thus k_β^1 and k_I^2

Table 1

Decomposition products of [NiBrRL$_2$] compounds in toluene solution under ethylene (30 bar)

| [NiBrRL$_2$]		Time [a]	T	% RC$_{2n}$	
R	L	(h)	(°C)	RC$_2$	RC$_4$
C$_6$Cl$_5$	PPh$_3$	8	90	45	55
C$_6$Cl$_5$ [b]	PPh$_3$	8	90	45	55
2,4,6-Me$_3$C$_6$H$_2$	PPh$_3$	2	25	75	25
2,4,6-Me$_3$C$_6$H$_2$	PPh$_3$ + freePPh$_3$ [c]	6	25	90	10
2,4,6-Me$_3$C$_6$H$_2$	PPh$_3$	2	90	90	10
2,4,6-Me$_3$C$_6$H$_2$	PMe$_2$Ph [c]	6	90	100	
2,4,6-Me$_3$C$_6$H$_2$	dppe [c]	6	90	100	
2,4,6-Me$_3$C$_6$H$_2$ [d]	PMe$_2$Ph	6	90	5	95
2,4,6-Me$_3$C$_6$H$_2$	PBz$_3$	2	65	40	60
2-MeC$_6$H$_4$	PPh$_3$	6	25	100	
3,5-Cl$_2$C$_6$H$_3$	PPh$_3$	6	25	100	
3,5-Cl$_2$C$_6$H$_3$	dppe	2	25	100	
2,3-Cl$_2$C$_6$H$_3$	PPh$_3$	6	90	90	~5
2,3-Cl$_2$C$_6$H$_3$	dppe [c]	6	25	100	
2,3-Cl$_2$C$_6$H$_3$	bipy [e]	6	90	–	–

[a] Total decomposition of the organometallic compound takes place unless otherwise indicated. [b] [{Ni(μ-Cl)(C$_6$Cl$_5$)(PPh$_3$)}$_2$]. [c] Starting complex partially recovered. [d] [Ni(2,4,6-Me$_3$C$_6$H$_2$)(C$_2$Cl$_3$)-(PMe$_2$Ph)$_2$], R = 2,4,6-Me$_3$C$_6$H$_2$. [e] Starting complex recovered.

(Scheme 1) are of the same order when R is bulky, but $k_\beta{}^2$ is always greater than $k_I{}^3$ in these conditions.

The differences between *cis* and *trans* complexes are less evident. Ethylene insertion into Pt–H [18] and Ni–C [19] bonds has been studied theoretically. The formation of an intermediate with a planar configuration involving the metal atom, the two carbon atoms of the olefin, and the alkyl group (or hydrogen atom) seems necessary. Consequently, a particular *cis* conformation of ligands is necessary. The rotation of the olefin is dependent on an energy barrier which is a function of the electronic effect of the *trans* ligand and steric interactions with the *cis* ligands. A phosphine *trans* to the olefin lowers the barrier to rotation whereas a halide raises it.

The geometry of *cis* complexes should be more favourable for the insertion process, assuming that the halide is labile, but, experimentally, *cis* complexes are less reactive towards insertion than *trans*. In a nonpolar solvent such as toluene, the position *cis* to R that must be occupied by ethylene to allow insertion is

Scheme 1.

[NiBrR(PPh₃)₂]
+
CH₃-CH=CH₂
8 bar

R = 2,4,6-Me₃C₆H₂

T = 90 °C

R = 3,5-Cl₂C₆H₃
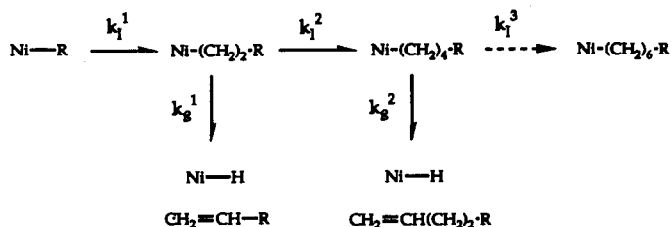
20%   80%
Ni → C₂   Ni → C₁
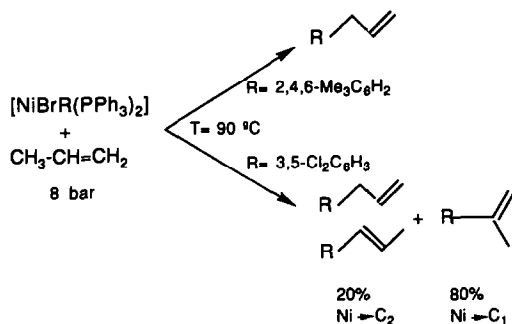
Scheme 2.

probably produced by loss of a phosphorus ligand. Reactivity should be related to phosphine lability, in a similar way to that reported for the alkyne insertion reaction with both monodentate and bidentate phosphines [20].

Accordingly, the insertion reaction in presence of free PPh_3 (Table 1) shows slower decomposition of the organometallic compound [2] and a decrease in the amount of the butenyl derivative produced after two consecutive insertions. Further, the low activation energy towards insertion for the most basic and crowded mesitylene ligand can only be explained by the dissociation of a phosphine ligand during the insertion process, since the substitution of the neutral ligand by ethylene is enhanced when the basicity of R increases. 3,5-Dichlorostyrene only was recovered from the reaction of the ionic compound [Ni(3,5-$Cl_2C_6H_3$)(γ-pic)dppe]ClO_4 in acetone solution at 25°C under 30 bar of ethylene. The reaction was complete in 24 h. This shows the lesser lability of bidentate phosphine in the cationic complex (see Table 1). Furthermore, the great inertness of the compounds containing *ortho*-chloroaryls may be related to the stability of the Ni–C bond in the presence of electronegative ligands plus induced the decrease in the lability of the phosphine.

Migratory-insertion of propene into the Ni–R bond

Reactions of propene with [NiBr(2,4,6-$Me_3C_6H_2$)(PPh_3)₂] and [NiBr(3,5-$Cl_2C_6H_3$)(PPh_3)₂], which are the compounds that react with ethylene under the mildest conditions only take place at 90°C in toluene, and with a different selectivity, which depends on the steric hindrance due to the group R. Thus, when R is the bulkiest ligand 2,4,6-$Me_3C_6H_2$, only Ni → C_2 addition is observed (Scheme 2). With 3,5-$Cl_2C_6H_3$, Ni → C_1 addition is favoured. This result suggests that rotation of the terminal double bond coordinated to the nickel atom before β-migration is severely restricted. Consistent with the transition states proposed for the β-migration process the conformation with R attached to Ni and the methyl group of the olefin placed as in Ia rather than as in Ib must be favoured. Furthermore, the steric effect of the mesitylene group allows β-elimination only from the methyl protons, giving the 3-(2,4,6-trimethylphenyl)propene. No subsequent isomerization was observed.

The ratio of the first and second insertions of the propylene is 18/82 for allyl nickel complexes with PPh_3 [2]. Furthermore, a ratio of 1/10 was observed in the

reaction between propene and [NiPh(acac)(PPh$_3$)] [21]. The different ratios observed with the complexes containing 2,4,6-Me$_3$C$_6$H$_2$ and 3,5-Cl$_2$C$_6$H$_3$ reported here are dependent on the size of the organic R group.


(1a)   (1b)
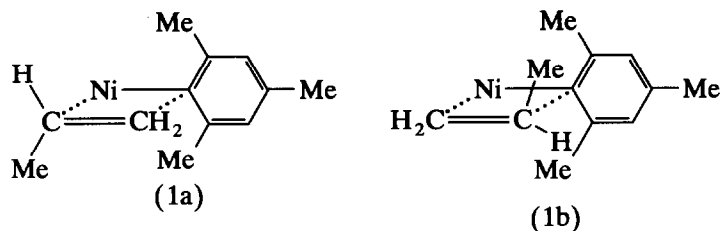
Detection of hydride intermediate

The isolation of the hydride intermediate from the mixtures in these reactions was impossible, probably due to the low stability of hydrides in conditions needed to activate the Ni–aryl bond. However a hydride was detected directly by ^{1}H NMR spectroscopy in the reaction of 0.15 g of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_3$)$_2$] in 10 ml toluene-d8 and ethylene at 20 bar at room temperature. After 30 min a signal of very low intensity assignable to the hydride was observed at -30.7 ppm in the spectrum recorded at 220 K. Therefore, the amount of hydride was extremely low.

It is also possible to use hydride-trapping reagents such as 3-butenyl-diphenylphosphine. Bennett *et al.* [22] observed the addition of a proton to a coordinated vinyl group (reaction 1). Wilke [23] reported hydride trapping by

$$+ \text{HBF}_4 \longrightarrow \qquad\qquad\qquad (1)$$

two isomers
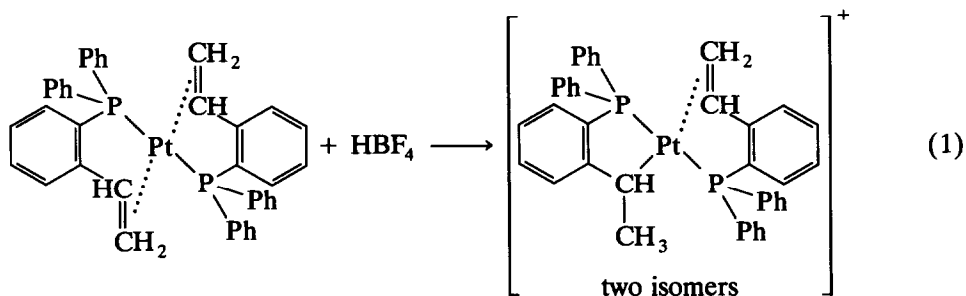
means of several 3-butenyl phosphines. The nickelacycle obtained is also five-membered [24]. Consequently we prepared [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_2$(3-butenyl))$_2$] and studied its reactivity in the presence of ethylene. Small amounts of butenes and decomposition products (phosphine oxides containing the 3-butenyl $z/e = 256$, 5-hexenyl $z/e = 284$, 7-octenyl $z/e = 312$ moieties) were observed when toluene solutions of the butenyl-containing complex were treated with 40 bar of ethylene at 70°C for 1 h. The analogous reaction at room temperature does not lead to butene. Isolation of a pure organometallic solid from the dark red-brown, highly air-sensitive solution was impossible. Since 2,4,6-trimethylstyrene was detected by GC, the doublet of doublets (47.0 and 22.3 ppm, J(PP) 278.3 Hz) observed in the ^{31}P{^{1}H} NMR spectrum of the toluene solution at -20°C showing two different *trans* phosphorus atoms may be explained by the formation of a nickelacycle, presumably five-membered, by addition of the hydride to the double bond of the phosphine (Scheme 3).
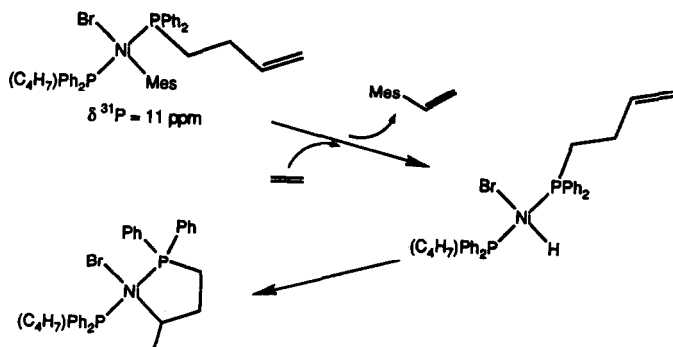
Scheme 3.

Dimerization ability

When solutions of [NiXRL$_2$] or [NiRL'L$_2$]Y were introduced into a Teflon liner placed in a reactor under ethylene pressure, mixtures of butenes in variable amounts were obtained (Table 2). Therefore, nickel hydride species may be responsible for the oligomerization of olefins when [NiXRL$_2$] or [NiRL'L$_2$]Y are used in this reaction.

Direct isolation of hydrides has been possible from some reaction mixtures [25], and several isolated hydrides have similar activity and selectivity to those of the non-hydridic organometallic precursors [17,26]. However, the hydrides are moderately stable and have *trans* phosphines and hydride *trans* to a halide (or oxygen).

Table 2

Dimerization of ethylene by [NiBr(2,4,6-Me$_3$C$_6$H$_2$)L$_2$] (runs 1–9) and [Ni(2,4,6-Me$_3$C$_6$H$_2$)L'L$_2$]BF$_4$ (runs 10–16) complexes

Run	L	L'	T (°C)	Conditions [a]	1-C$_4$ (%)	trans-2-C$_4$ (%)	cis-2-C$_4$ (%)	Turnover [C4]/[Ni]
1	P(^{n}Bu)$_3$		65		74	11	15	89
2	P(^{i}Bu)$_3$		65		21	51	28	250
3	PBz$_3$		65		24	18	58	700
4	PEt$_3$		65		98	1	1	43
5	PEt$_3$		80	c,d	58	20	22	20
6	PPh$_3$		25	c,d	80	5	15	55
7	1/2DPPE		80	c,d	50	22	28	5
8	1/2PN [b]		80	c	–	–	–	–
9	1/2bipy		80	c	–	–	–	–
10	P(^{n}Bu)$_3$	MeCN	65	e	35	40	25	1150
11	P(^{n}Bu)$_3$	MeCN	65		59	27	14	2430
12	P(^{i}Bu)$_3$	MeCN	30		90	7	3	2750
13	PBz$_3$	MeCN	30		91	5	4	5000
14	PMe$_2$Ph	MeCN	65		96	3	1	30
15	1/2PN [b]	THF	85		–	–	–	f
16	1/2dppe	py	85		–	–	–	g

[a] Standard conditions: ethylene 40 bar, in THF, 2 h. [b] PN = Ph$_2$PCH$_2$(2-C$_5$H$_4$N). [c] In toluene. [d] 4 h. [e] 20 bar. [f] 2,4,6-trimethylstyrene detected. [g] Small amounts of polyethylene obtained, 2,4,6-trimethylstyrene not observed.

Scheme 4.

Neutral Compounds : X= Halide, n= 0
Ionic Compounds : X= PR$_3$, n= 1
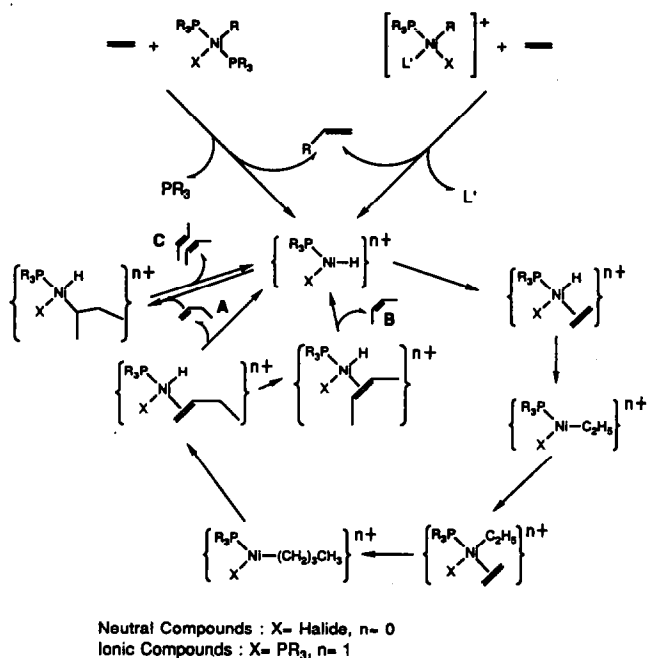
This arrangement does not seem to be optimal for easy insertion of olefin in the active catalytic species. The actual active intermediate is probably slightly different.

We can draw conclusions from our results. The active intermediate is a nickel hydride, which may or may not contain another anionic ligand (halide) depending on whether the precursors are neutral or ionic. This quite different activity of neutral and ionic compounds suggests that dissociation of the halide is unlikely in neutral compounds. At least one and probably two phosphines remain bonded judging from the changes in activity and selectivity shown with the change of the phosphine. Dissociation of one phosphine may occur from the neutral complexes, but is unlikely from the ionic compounds. Furthermore, very different selectivities, far from the thermodynamic equilibrium mixtures of butenes, are observed with the most active ionic compounds, showing the effect of the coordinated phosphines. Moreover, these ionic compounds have a labile non-phosphorus ligand that ensures the necessary free coordination position.

The activity observed can be related to the stability of the hydride intermediate [17]. The lack of activity in the compounds containing neutral bidentate ligands may relate to the known instability of these hydrides, and also to the lack of free coordination positions.

The selectivity observed in the dimerization to butenes is unusual and at least three patterns are observable, indicated by A, B and C in Scheme 4. The thermal decomposition by β-hydride elimination of complexes cis-[PtX(n-C$_4$H$_7$)(PEt$_3$)$_2$] in conditions where isomerization is completely blocked [27] was interpreted in terms of a pentacoordinate [Pt(H)X(olefin)L$_2$] intermediate. The simultaneous formation

of three olefin isomers, 1-butene, *cis*-2-butene and *trans*-2-butene, suggests that the release of organic products must be preceded by a preequilibrium that allows an easy skeletal isomerization of linear to branched alkyl groups [27,28]. It was also reported that the relative proportion of 1-butene and *cis*-2-butene is dependent on the ligand X, but the amount of *trans*-2-butene produced is lower than 5% in all cases and does not change significantly with X.

Related behaviour could explain the result obtained with the neutral compound containing PBz_3 (run 3 in Table 2), mode **B** in Scheme 4. In neutral or ionic compounds with less bulky phosphines, the coordination of 1-butene may compete with ethylene in the stable active intermediate, and isomerization may take place, leading to a mixture of butenes related to the thermodynamic ratio (runs 2 and 10, Table 2), mode C for isomerization. When the hydride species is unstable (runs 4 and 14) or the crowding of the ligand is large enough to hinder internal reorganizations or butene coordination (runs 12, 13), formation of 1-butene is selective (mode A).

Alkyl species have been detected spectroscopically in the solutions of homogeneous Ni systems, $[NiR(AB)L]$, AB = 2,4-pentandienate [29] or Ph_2PCH_2COO [11]. Further, alkyl-ethylene complexes have been detected in cyclopentadienyl derivatives of Ni [30], Co [31] and Rh [32]. This has allowed the estimation of free energies of activation for β-migratory insertions of M–H or $M-C_2H_5$ to ethylene [32]. These results showed higher barriers for migrations to alkyl than for hydride migrations. Nevertheless we did not detect unambiguously these intermediates.

Experimental

Infrared spectra were recorded on a Perkin–Elmer spectrophotometer. ^1H and ^{31}P NMR spectra were obtained using either a Varian XL-200 (^1H: 200 MHz) or a Bruker WP80SY (^{31}P: 32.4 MHz) spectrometer. Chemical shifts are referred to Me_4Si or H_3PO_4 (85%) and reported in ppm with positive values downfield relative to the reference. GC analyses were performed either on a Hewlett-Packard 5710A instrument equipped with a 9-m stainless-steel column packed with 23% SP-1700 on 80/100 Chromosorb P AW and connected to an HP 3390 A integrator for butene identification, or on a Hewlett-Packard 5890 connected to an HP 3396A integrator equipped with a 25 m ultra-2 cross-linked 5% phenylmethyl silicone capillary column.

All solvents were purified by standard methods. THF was distilled over sodium benzophenone under dinitrogen before use. Phosphines were purchased or prepared according to published procedures [33]. 2-[(Diphenylphosphino)methyl]pyridine was obtained as described by B. Akermark *et al.* [34]. Ethylene (L'air liquide 99.95%) was used as received.

Preparations

Neutral complexes
$[NiBr(polychlorophenyl)P_2]$ and $[NiBr(2,4,6-Me_3C_6H_2)P_2]$ (P = PEt_3, PMe_2Ph, PPh_3, $P(^nBu)_3$, $P(^iBu)_3$, PCy_3 or PBz_3) were obtained by published methods [17]. Every preparative manipulation was performed under dinitrogen.

As an example, [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PBz$_3$)$_2$] was obtained by slow addition of mesitylmagnesium bromide in THF to a suspension of [NiBr$_2$(PBz$_3$)$_2$] (0.5 g) in THF (20 ml) at room temperature. Addition was stopped when the colour of the solution changed from red-orange to yellow. Upon cooling to 0°C, a yellow precipitate of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PBz$_3$)$_2$] was obtained. Addition of absolute ethanol improved the precipitation. The compound was recrystallized from CH$_2$Cl$_2$ ethanol. Yield: 60% (0.6 g). Analytical data (found (calc.) (%)): C, 69.8 (70.7); H, 6.1 (6.2).

[NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_2$CH$_2$(2-py))]. 0.42 g (1.5 mmol) of 2-[(diphenyl-phosphino)methyl]pyridine was added to a solution of 1.2 g (1.5 mmol) of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_3$)$_2$] in 60 ml of toluene. After 1 h stirring at room temperature a yellow precipitate was obtained. The yield was 60% (0.48 g). Analytical data (found (calc.) (%)): C, 60.6 (60.25); H, 5.1 (5.25); N, 2.6 (2.43). $\delta(^{31}P)$: 30 ppm at room temperature in toluene. $\delta(^{1}H)$: 2.62 (2,4-Me), 2.06 (6-Me) in CDCl$_3$ at room temperature.

[NiBr(2,3-Cl$_2$C$_6$H$_4$)L–L] *(L–L = dppe, bipy)*. 1.1 mmol (0.5 g of dppe or 0.17 g of bipy) was added to a solution of 1 mmol (0.808 g) of [NiBr(2,3-Cl$_2$C$_6$H$_3$)(PPh$_3$)$_2$] in 20 ml of toluene at room temperature. When L–L is dppe the yellow solution became orange and a solid appeared after 30 min stirring. The precipitate of [NiBr(2,3-Cl$_2$C$_6$H$_4$)dppe] was filtered off. Yield 80% (0.55 g). Analytical data (found (calc.) (%)): C, 57.3 (56.26); H, 4.0 (3.98). When bipy is added, 3 h stirring are necessary to complete the reaction. After cooling to −70°C, the red precipitate was filtered off, washed with 1% HCl aq., and dried under reduced pressure. Yield: 75% (0.3 g). Analytical data (found (calc.) (%)): C, 47.2 (48.48); H, 3.0 (2.80); N, 7.3 (7.06).

[NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_2$(CH$_2$CH$_2$CH=CH$_2$))$_2$]. 6 ml of a 0.15 M solution of 3-butenyldiphenylphosphine was added to a solution of 0.323 g (4 mmol) of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_3$)$_2$] in 20 ml of toluene. The mixture was heated under reflux for 3 h. Then it was concentrated at low pressure and *iso*-propanol was added. On cooling to −10°C a yellow precipitate of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_2$ (CH$_2$CH$_2$CH=CH$_2$))$_2$] was obtained. Yield: 50% (0.37 g). $\delta(^{31}P)$ 11 ppm. Analytical data (found (calc.) (%)): C, 65.9 (66.45); H, 6.0 (6.14).

Ionic complexes

[Ni(2,4,6-Me$_3$C$_6$H$_2$)(py)(dppe)]BF$_4$. 0.2 g (1 mmol) of AgBF$_4$ was added to a solution of 0.1 g (1.3 mmol) of pyridine and 0.65 g (1 mmol) of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(dppe)] in 30 ml of THF. After 30 min stirring the suspension was filtered and collected in 20 ml of toluene. After cooling to −10°C overnight a yellow precipitate was obtained. The yield was 50% (0.37 g). Analytical data (found (calc.) (%)): C, 66.8 (64.34); N, 1.7 (1.87); H, 5.6 (5.36). $\delta(^{31}P)$ 49.57(d) and 36.49(d) ppm, $J(PP')$ 8.6 Hz.

[Ni(2,4,6-Me$_3$C$_6$H$_2$)(THF)(PN)]BF$_4$. 0.02 g (0.1 mmol) of AgBF$_4$ was added to a solution of 0.0535 g (0.1 mmol) of [NiBr(2,4,6-Me$_3$C$_6$H$_2$)(PPh$_2$CH$_2$(2-py))] in 20 ml of THF. The suspension was filtered and the clear solution containing the ionic compound was used in the reactor.

Ethylene reactions

Ethylene reactions were performed on a Berghof reactor of 100 ml capacity equipped with a magnetic stirring bar, two gas valves, a manometer and a

thermocouple. One of the gas valves allowed direct introduction of the solution *via* syringe, which may be deposited on a Teflon liner, on a glass vessel in the Teflon liner, or directly on the steel. No significant change was observed when the type of container was changed.

A solution of ~ 50 mg of the neutral or ionic complex in 15 ml of THF was prepared under N_2 atmosphere. The solution was transferred *via* syringe under argon into the Berghof autoclave which had been previously purged. Ethylene was introduced until the desired initial pressure was achieved and the required temperature for the experiment was then obtained with a heating mantle. After the time indicated for each reaction at the desired temperature, the reactor was cooled to $-20°C$ and slowly vented. The distribution of RC_2 and RC_4 or C_4 and C_6 fractions was determined by GLC analysis.

Acknowledgment

References

1 (a) W. Keim, A. Behr and A. Roper, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press, Oxford, UK, 1982, p. 373; (b) P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol II, Academic Press, London, UK, 1975.
2 J. Skupinska, Chem. Rev., 91 (1991) 613.
3 Y. Ishimura, K. Maruya, Y. Nakamura, T. Mizoroki and A. Ozaki, Bull. Chem. Soc. Jpn., 56 (1983) 818; T. Koike, T. Kawakami, K. Maruya, T. Mizoroki and A. Ozaki, Chem. Lett., (1977) 551.
4 K. Maruya, T. Mizoroki and A. Ozaki, Bull. Chem. Soc. Jpn., 43 (1970) 3630.
5 J. Brunet, A. Sivade and I. Tkatchenko, J. Mol. Catal., 50 (1989) 291.
6 E. Balbolov, M. Mitkova, K. Kurtev, J. Gehrke and R. Taube, J. Organomet. Chem., 352 (1988) 247.
7 B. Bogdanovic, B. Spliethoff and G. Wilke, Angew. Chem., Int. Ed. Engl., 19 (1980) 622.
8 M. Uchino, K. Asagi, A. Yamamoto and S. Ikeda, J. Organomet. Chem., 84 (1975) 93.
9 A. Tenaglia, E. Terranova and B. Waegell, J. Mol. Catal., 40 (1987) 281.
10 G. Wilke, Proc. 5th IUPAC Symp. Org. Synth. 1984, Blackwell Scientific Publications, Oxford, UK, 1985, p. 1.
11 M. Peuckert and W. Keim, Organometallics, 2 (1983) 594.
12 S.J. Brown and A.F. Masters, J. Organomet. Chem., 367 (1989) 371.
13 R.B.A. Pardy and I. Tkatchenko, J. Chem. Soc., Chem. Commun., (1981) 49.
14 J.R. Ascenso, A.R. Dias, P.T. Gomes, C.C. Romao, Q. Pham, D. Neibecker and I. Tkatchenko, Macromolecules, 22 (1989) 998.
15 P. Cossee, J. Catal., 3 (1964) 80; E.J. Arlman and P. Cossee, J. Catal., 3 (1964) 99.
16 U. Klabunde and S.I. Ittel, J. Mol. Catal., 41 (1987) 123.
17 R.M. Ceder, G. Muller, J. Sales, J. Vidal, D. Neibecker and I. Tkatchenko, J. Mol. Catal., 68 (1991) 23.
18 D.L. Thorn and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 2079.
19 B.M. Trzcinska, J.P. Fackler and A.B. Anderson, Organometallics, 3 (1984) 319.
20 J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 3002.
21 K. Maruyama, T. Ito and A. Yamamoto, J. Organomet. Chem., 155 (1978) 359.
22 M.A. Bennett, C. Chiraratvatana, G.B. Robertson and U. Tooptakong, Organometallics, 7 (1988) 1394.
23 G. Wilke, Angew. Chem. Int. Ed. Engl., 27 (1988) 185.
24 T. Yamamoto, K. Sano and A. Yamamoto, J. Am. Chem. Soc., 109 (1987) 1092; E. Lindner, G. Funk and S. Hoehne, J. Organomet. Chem., 214 (1981) C7.
25 U. Müller, W. Keim, C. Krüger and P. Betz, Angew. Chem., Int. Ed. Engl., 28 (1989) 1011.
26 W. Keim, J. Mol. Catal., 52 (1989) 19.

27 G. Alibrandi, L.M. Scolaro, D. Minniti and R. Romeo, Inorg. Chem., 29 (1990) 3467.

28 R.L. Brainard and G.M. Whitesides, Organometallics, 4 (1985) 1550.

29 G.T. Crisp, S. Holle and P.W. Jolly, Z. Naturforsch., Teil B, 37 (1982) 1667.

30 H. Lehmkuhl, Pure Appl. Chem., 58 (1986) 495; H. Lehmkuhl *et al.*, Chem. Ber., 117 (1984) 3231; H. Lehmkuhl in A. Meijere, H. tom Dieck (Eds.), Organometallics in Organic Synthesis, Springer Verlag, Berlin, 1988.

31 M. Brookhart, A.F. Volpe, D.M. Lincoln, I.T. Horváth and J.M. Millar, J. Am. Chem. Soc., 112 (1990) 5634.

32 M. Brookhart and D.M. Lincoln, J. Am. Chem. Soc., 100 (1988) 8719.

33 G.M. Kosolapoff and L. Maier, Organic Phosphorus Compounds, Wiley, New York, 1972, Vol. 1.

34 B. Akermark, B. Krakenberger, S. Hansson and A. Vitagliano, Organometallics, 6 (1987) 620.