Diphosphines with Expandable Bite Angles: Highly Active Ethylene Dimerisation Catalysts Based on Upper Rim, Distally Diphosphinated Calix[4]arenes

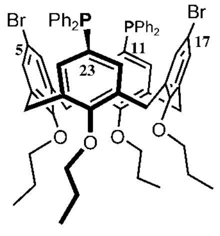
Manuel Lejeune,[a] David Sémeril,[a] Catherine Jeunesse,[a] Dominique Matt,*[a] Frédéric Peruch,[b] Pierre J. Lutz,*[b] and Louis Ricard[c]

Abstract: The binding properties of two large diphosphines, *cone*-5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**1**) and *cone*-5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**2**) toward Ni^{II} centres have been investigated. Whatever the starting complex, $NiBr_2$ or $[NiCp]BF_4$, quantitative formation of a chelate complex was observed, illustrating the preorganisation of the ligands. An X-ray structure determination was carried out for $[NiCp\cdot\mathbf{1}]BF_4$ which revealed that the nickel atom is positioned to one side of the calixarene axis, the PNiP plane being roughly parallel to the calixarene reference plane. The molecule has C_1 symmetry in the solid state, a feature which is also observed in solution at low temperature. As shown by variable-temperature ^1H and ^{31}P NMR studies, the complex undergoes two distinct motions: 1) a fan-like swinging of the coordination plane which displaces the metal from one side of the calixarene axis to the other, a motion during which the PNiP angle is likely to undergo a significant enlargement; 2) a rapid oscillation of each PPh_2 unit about the corresponding Ni−P bond. In the latter dynamics the two *endo*-oriented PPh rings alternately occupy the calixarene entry. The two flexible ligands were assessed in ethylene oligomerisation. Activation with methylaluminoxane of the paramagnetic complexes $[NiBr_2\cdot(\mathbf{1}\text{ or }\mathbf{2})]$ afforded highly active ethylene dimerisation catalysts, with turnover frequencies up to $10^6\,(\text{mol }C_2H_4)(\text{mol Ni})^{-1}\,h^{-1}$. The selective formation of 1-butene can be rationally controlled by using low catalyst concentrations.

Keywords: calixarenes • ethylene dimerisation • molecular dynamics • nickel • P ligands

Introduction

Generic calix[4]arenes provide exceptionally useful platforms for the preparation of multidentate ligands with convergent binding sites.[1–6] Despite the widespread applications of such multitopic ligands in supramolecular chemistry,[7–10] the use of calixarenes in catalytic chemistry is only in its infancy.[11–24] Recently, methodology has become available that allows regioselective attachment of two phosphino groups to the upper rim of calix[4]arenes immobilised in the *cone* conformation, resulting either in distally[25,26] (calixarenes with substitution patterns as in **1** or **2**) or proximally[22,27,28] functionalised (i.e. 5,11-substituted) compounds. Both types of diphosphine were shown to form transition-metal complexes, but interestingly only the distally functionalised compounds appear suitable for the formation of complexes involving chelate rings. For example, the latter ligands form octahedral ruthenium complexes of *trans*-configuration, a property that can be used for the controlled posi-



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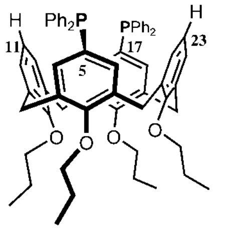

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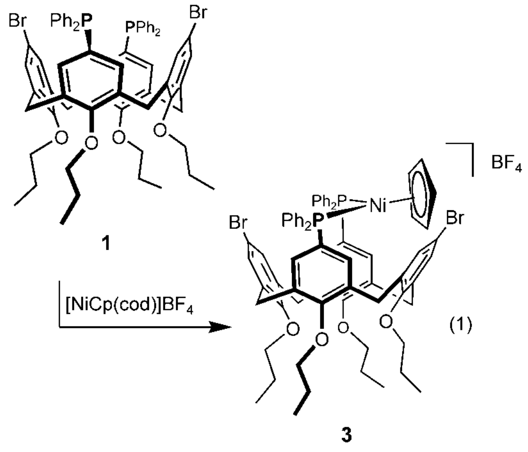
DOI: 10.1002/chem.200400492

tioning of metal-organic fragments inside the calix cavity.[25] In contrast, *cis*-chelating behaviour of these 12-membered ligands, as observed with square-planar Pd^{II} or Pt^{II} metal centres, displaces the metal away from the calixarene axis, the coordination plane adopting an orientation which is almost parallel to the calixarene reference plane.[26] Thus, while important aspects of the coordination chemistry of these ligands have already been considered, no study of the catalytic properties of such distally diphosphinated calixarenes has yet been made. Herein we report for the first time the preparation of Ni-based precatalysts which turned out to be *highly* active ethylene dimerisation catalysts. It is worth mentioning that the two ligands used in this study are thermally robust, making them particularly interesting for catalytic applications. The electronic properties of the P^{III} atoms, as inferred from the ^{31}P NMR data ($\delta(^{31}P) = -6.6$ ppm (**1**); -6.4 ppm (**2**)), are close to those of triphenylphosphine. Hence **1** and **2** may be regarded as chelators containing two independent triphenylphosphine coordination centres.

Results and Discussion

Synthesis and dynamics of nickel(II) complexes obtained from 1 and 2: The two calixarene ligands used in this study have been prepared according to a previously described method. Reaction of $[Ni(\eta^5\text{-}C_5H_5)(cod)]BF_4$ (cod = 1,5-cyclooctadiene) with diphosphine **1** produced the diamagnetic, yellow complex **3** in high yield [Eq. (1)]. Chelate formation was inferred from the electron spray mass spectrum which showed an intense peak at 1241 (with the expected isotopic profile), corresponding to the $[M-BF_4]^+$ ion.



The molecular structure of **3** was determined by a single X-ray diffraction study. The unit cell contains two very similar molecules, **3a** and **3b**, each with C_1 symmetry (Figure 1; Table 1). The calixarene units adopt a flattened *cone* conformation,[29] with the two phosphorus-bearing phenol rings being markedly displaced towards the interior of the cavity upon complexation (dihedral angle: $-28.2°$ (**3a**), $-26.8°$ (**3b**); versus $+57.7°$ (**3a**) and $+63.6°$ (**3b**) for the other two distal rings). As already observed in the previously reported complex $[PtCl_2{\cdot}\mathbf{1}]$, chelation positions the metal atom away from the calixarene axis, with one side of the coordination plane facing the cavity interior. In the two isomers the dihedral angle between the PNiP plane and the calixarene reference plane (defined as the mean plane of the bridging ArCH_2 carbon atoms) is only about 20°. The bite angle of the chelating unit, 104.72(6)° (**3a**) and 103.69(5)° (**3b**), is rather large but is comparable with that found in other complexes of the general formula $[NiCp(PPh_3)_2]^+$ (Cp = C_5H_5 or Cp-derived ligand).[30] In *cis*-$[PtCl_2{\cdot}\mathbf{1}]$, the bite angle is sig-

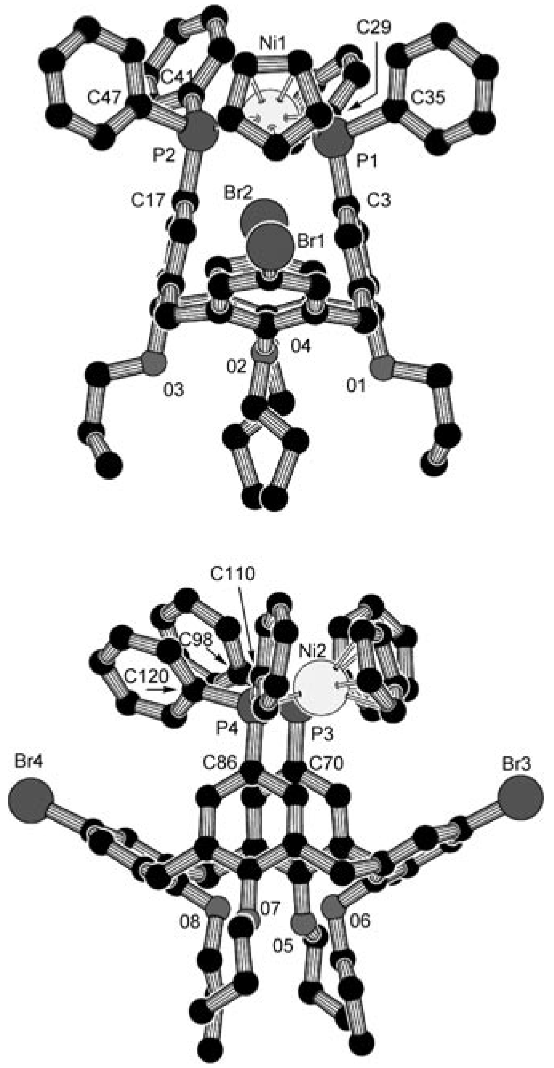


Figure 1. Molecular structure (Platon) of **3a** (top) and **3b** (bottom).

Table 1. Selected bond lengths [Å] and angles [°] for **3.**

Distances			
Ni1–P1	2.207(2)	Ni1–P2	2.184(2)
Ni2–P3	2.212(2)	Ni2–P4	2.185(2)
P1–C29	1.834(5)	P2–C41	1.822(5)
P3–C98	1.825(6)	P4–C120	1.822(5)
Angles			
P2-Ni1-P1	104.72(6)	P4-Ni2-P3	103.69(5)
C98-P3-Ni2	116.8(2)	C120-P4-Ni2	116.1(2)
C70-P3-C98	105.0(2)	C120-P4-C86	112.2(2)
C41-P2-Ni1	117.0(2)	C29-P1-Ni1	119.3(2)
C3-P1-C29	104.5(2)	C41-P2-C17	111.5(2)

nificantly smaller, 99.7°, thus illustrating the flexibility of the calixarene scaffold in adapting to the electronic requirements imposed by the metal centre. As already mentioned, each isomer contains a single PPh ring oriented towards the centre of the cavity (ring C29 in isomer **3a**, and its counterpart C120 in isomer **3b**), making the two phosphorus atoms of each isomer inequivalent. The asymmetry of the whole structure can be seen by comparing the two angles C17-P2-C41 and C3-P1-C29 (111.5(2)° and 104.5(2)°, respectively) as well as the Ni–P bond lengths (Ni1–P2 2.1839(15); Ni1–P1 2.2073(15) Å). The inequivalence of the P atoms is also evident in solution at low temperatures. Thus, the ^{31}P NMR (CD_2Cl_2, 202.45 MHz) spectrum measured at 200 K shows an AB quartet with $^2J(P,P') = 42$ Hz (Figure 2). As the temperature is increased the two phosphorus signals first broaden then coalesce near 268 K, and finally merge to a single signal. This observation is best interpreted in terms of a fast oscillation of the two PPh_2 units about their respective P–Ni bonds, a motion that takes alternately each of the *endo*-phenyl rings from directly above towards one side of the cavity (Scheme 1). The activation barrier[31] for this exchange is 11.4 kcal mol^{-1}. Interestingly, the ^{1}H NMR spectra measured at low temperatures (Figure 3) show four distinct AB quartets for the $ArCH_2Ar$ protons, in keeping with the C_1-symmetrical structure already observed in the solid state. As the temperature is raised, these signals simplify to a single AB quartet, indicating the molecule to have effectively a C_{2v}-symmetrical structure. The latter findings not only corroborate the conclusions drawn from the ^{31}P NMR study, but also imply that the metal plane undergoes a fan-like motion during which the nickel atom is displaced from one side to the other of the calix axis (Scheme 1). Similar conclusions have been drawn previously for the related complexes *cis*-[PtCl$_2$·**1**] and [Pd(Me-allyl)·**2**]BF$_4$, but in these complexes the fanning motion could not be frozen out. Analysis of the ^{1}H NMR spectra did not enable features specific for each motion to be identified, the energy barriers of the two processes being too close. The $\Delta G^{\#}$ value determined for the process having the lowest barrier was 11.2 kcal mol^{-1} (cf. 11.4 kcal mol^{-1} for the $\Delta G^{\neq}$ value, as inferred from the ^{31}P NMR variable-temperature study). Regarding the swinging of the coordination plane, the stereochemistry of the nickel atom in the transition state is a matter of contention. We do not know how

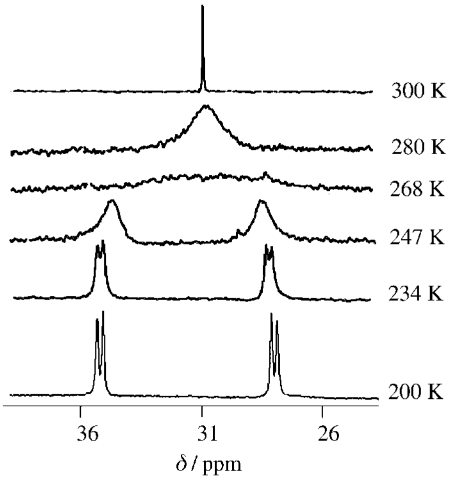


Figure 2. ^{31}P NMR (CD_2Cl_2) variable-temperature study of **3**.

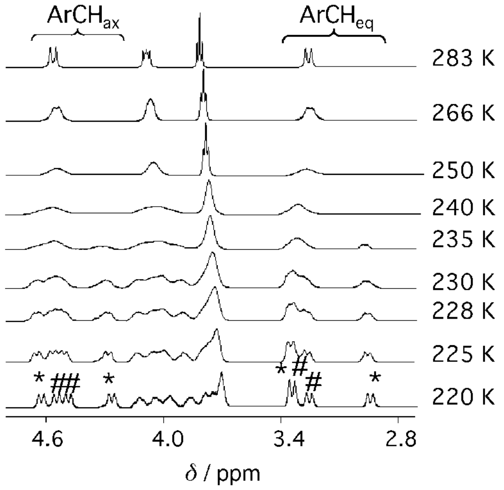
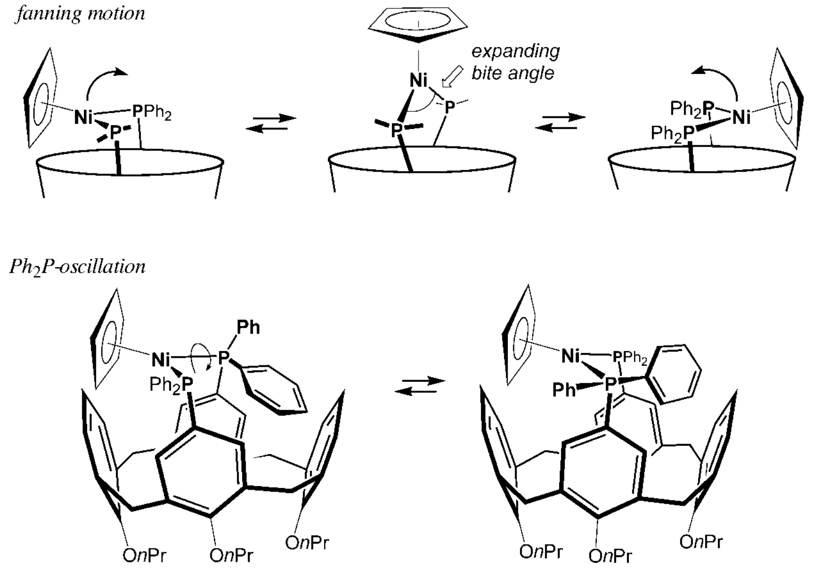


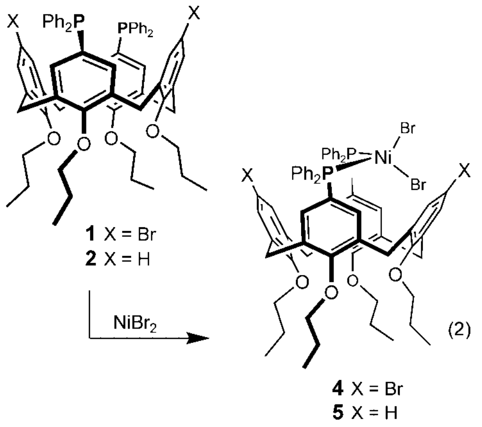
Figure 3. ^{1}H NMR (CD_2Cl_2) variable-temperature study of **3** ($ArCH_2$ region). Equilibrating ArCH$_{ax}$ or ArCH$_{eq}$ protons are marked by the symbols * and #, respectively.



Scheme 1. Dynamics of complex **3** in solution. Top: fanning motion displacing the metal centre from one side of the calixarene axis to the other. Bottom: reversible, restricted rotation about the Ni–P bonds.

the metal coordination geometry varies when the metal plane swings from one side to the other, in particular what is the P-Ni-P angle in the transition state. The rather normal value of the J(P-P′) constant determined for the slow exchange indicates that during the motion, the P atoms are likely to remain coordinated in a *cis* fashion. Molecular mechanics calculations using SPARTAN were carried out assuming that the only stereochemical parameter which varies is the P-Ni-P angle.[32] With this hypothesis, the calculated energy barrier for the fanning motion is about 12 kcal mol^{-1}, with a P-Ni-P angle raising up to 124°. This $\Delta G^{\neq}$ value fits well with our experimental data. It is worth mentioning here that our findings about the dynamic behaviour of **3** are fully consistent with those of Tsuji et al. who recently reported on a square-planar Pt^{II} chelate complex based on a related ligand, although the latter is bearing heavier substituents.[33] Interestingly, these authors describe the motion which equilibrates the P atoms as resulting from a reversible twist of the calixarene backbone, this interpretation being deduced from calculated dihedral P-C$_{calix}$···C$_{calix}$-P angles of about 11°. The corresponding angles in **3a** and **3b** being respectively of only 2.4° and 3.3° in the solid state, the P1/P2 exchange in this complex is therefore better described as a simple oscillation about the P–Ni bond. This description is also consistent with the fact that a single *endo*-oriented P-phenyl ring occupies the calixarene entrance.

The complex **4** was obtained in high yield by reacting anhydrous NiBr$_2$ with **1** in CH$_2$Cl$_2$ [Eq. (2)]. The green colour and the observed paramagnetism of this complex is consistent with a tetrahedral coordination geometry. The molecular formula of **4** was inferred from elemental analysis and an osmometric molecular weight determination (see Experimental Section). The related complex **5**, also paramagnetic, was prepared in a similar way. Despite several attempts to obtain single crystals of these complexes, the solid state structure of neither could be determined. Thus, the precise orientation of the chelating unit in the solid state is not known, but as shown by molecular modeling, the strain of this molecule may be minimized if the tetrahedral nickel atom is displaced away from the calixarene axis. We therefore assign a sidewards orientation of the metal atom, as already established for complex **3**.



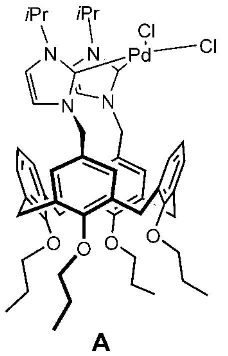
Oligomerisation of ethene: Complexes of the type [NiX$_2$(diphosphine)] (X = halide), once activated with alkylaluminium compounds, constitute effective catalytic systems for olefin oligomerisation or polymerisation.[34–37] It is well known that the performances of such systems mainly depend upon the nature of the phosphine used.[38] In the present study, complexes **4** and **5** were activated with 400 equivalents of methylaluminoxane (MAO). The runs were carried out in a 100-mL steel autoclave under an ethylene pressure of 20–30 bar with toluene as solvent. The whole autoclave was cooled by means of an ice bath. In the present study the chelate complex [NiBr$_2$(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) was used as reference (Table 2, run 1). In each test the reaction started as soon as an ethylene pres-

Table 2. Catalytic ethylene dimerisation in a 100-mL steel autoclave.[a]

Run	Precursor	n(Ni) [µmol]	t [h]	P(C$_2$H$_4$) [bar]	T [°C]	ΔT[b] [°C]	MAO [equiv/Ni]	yield [g][c]	TOF[d]/10^{-4}
1	NiBr$_2$(dppe)	4.5	0.25	30	40	13	400	1.07	3.39
2	**4**	4.5	1	30	10	3	400	2.44	1.93
3	**4**	4.5	0.25	30	25	5	400	4.27	13.54
4	**4**	4.5	0.5	30	25	5	400	5.94	9.42
5	**4**	4.5	1	30	25	5	400	7.00	5.55
6	**4**	4.5	0.25	20	25	5	400	1.90	6.03
7	**4**	4.5	0.25	30	40	40	400	2.63	8.34
8	**4**	4.5	1	30	40	40	400	3.54	2.81
9	**4**	1.5	1	30	40	5	400	1.20	2.85
10,11[e]	**4**	0.09	0.25	20	25	3	400	0.76	120.54
12	**4**	0.09	0.25	20	25	3	10000	0.61	96.75
13	**4**	0.09	0.25	20	25	3	20000	0.40	63.44
14	**5**	4.5	0.25	20	25	57	400	3.70	11.74
15–17[e]	**5**	0.09	0.25	20	25	3	400	0.52	83.53
18	**5**	0.81	0.25	20	25	3	400	0.95	16.74
19	**5**	0.81	0.25	20	25	3	1260	1.45	25.55
20	**3**	4.5	1	30	40	3	1000	2.92	2.31

[a] Toluene 22 mL, 500 rpm. [b] Max. temperature increase (°C) during the catalytic run. [c] Yield determinated by mass of final reaction mixture versus mass of control reaction in toluene (22 mL). [d] Mol of C$_2$H$_4$ converted per mol of Ni per hour ((mol C$_2$H$_4$)(mol Ni)$^{-1}$ h^{-1}). [e] For these experiments the results were averaged.

sure was applied, producing sometimes a considerable temperature increase (up to 57 °C, see Table 2, entry 14). Both complexes turned out to be excellent dimerisation catalysts, displaying higher activities than $[NiBr_2(dppe)]$ (Table 2). The observed butene selectivities were all larger than 95 %. The optimal reaction temperature was found to be 25 °C. We noted some important differences between the two complexes. Thus, when using an amount of 4.5 μmol of catalyst (in 22 mL of toluene) the activity of complex **5** was about two times higher than that observed with **4** (compare for example runs 6 and 14 in Table 2). The better performance of **5** could be due to steric reasons: MAO possibly interacts with the calixarene-bonded Br atoms of **4** resulting in a calixarene bearing very bulky substituents that make the metal environment more crowded, hence reducing its activity. It is worth mentioning here that at this catalyst concentration, a fast temperature increase was observed with **5** (the temperature reaching 82 °C for an initial ethylene pressure of 20 bar), causing a loss of activity after a few minutes. Under similar conditions complex **4** remained active, the reaction temperature remaining below 35 °C. Catalyst decomposition induced by a rapid temperature increase has already been reported for other Ni-based ethylene oligomerisation catalysts.[39,40] The observed exothermicity also caused an isomerisation of 1-butene into 2-butenes. This phenomenon is not new either.[41] In run 6 for example, 1-butene and 2-butenes were formed in a 25:75 ratio. To maintain the activity of **5** over a longer period, and incidentally also produce mainly 1-butene, we carried out a catalytic run using a 50-fold lower concentration (Table 2, runs 15–17). In this case the reaction temperature could be kept near room temperature and accordingly, no loss of activity was observed. The proportion of 1-butene was then 91 %, hence demonstrating that temperature control of the reaction can drastically reduce the 1-butene isomerisation. The highest TOF observed with **5** reached $0.83\times10^{6}\,h^{-1}$, which corresponds to the *highest* dimerisation activity ever observed for $[NiX_2(diphosphine)]$ complexes.[36,37,42] Thus, the lifetime of the catalytically active species seems to be strongly dependent on the temperature which should not exceed 30 °C. At temperatures near 25 °C, the catalyst indeed displayed a longer lifetime, remaining active after 1 h, although the catalyst activity slowly decreased. The high activity of complex **5** probably relies on the particular features of the diphosphine ligand. It appears likely that during the dimerisation process a rapid fan-like motion of the P-Ni-P plane, as described above for complex **3**, still takes place, resulting in a permanent variation of the ligand bite angle. A moderate increase of the ligand bite angle possibly reduces the activation barrier of the reductive elimination step in the dimerisation process, hence leading to a faster olefin dimerisation. Preliminary studies showed that other C–C coupling reactions carried out with **4**, for instance norbornene polymerisation, also led to remarkably high activities when compared to that of other $[NiBr_2(diphosphine)]$ procatalysts (see Experimental Section). A possible bite angle variation during the catalytic process which lowers the activation barrier of the rate-determining step may here again be invoked. Interestingly, in a recent study, Schatz et al. described the use of the calixarene-bis(carbene)palladium(II) complex **A** for Suzuki cross-coupling reactions.[24] Like in complexes **3**–**5**, the chelating unit in these calixarenes positions the catalytic centre away from the calixarene axis, but in the molecules developed by Schatz and co-workers the capping unit is more rigid, thus preventing displacement of the metal centre from one side to the other. Interestingly, these bis(carbene) ligands do not lead to an unusual activity increase. Of course, whether this arises from the ligand's rigidity cannot be stated with certainty, in particular because the mecanisms involved in ethylene dimerisation and Suzuki cross coupling cannot strictly be compared.



A

Complex **4** was also tested under "high dilution" conditions and, unexpectedly, its activity surpassed then that of **5**, the activity rising up to $1.2\times10^{6}\,h^{-1}$ (runs 10,11). The higher activity of **4** versus **5** under these conditions could arise from the fact that most MAO was used for cleaning the reaction medium (note, in these runs only 1.78 mg of MAO was present in the 100-mL autoclave), hence leaving the Br atoms of the calixarene unmodified. The halide atoms are thus able to interact with the terminal methyl group of an intermediately formed Ni-butyl moiety, a situation which possibly favors β-elimination through an in-plane positioning of the β-H atom. The beneficial role of neighbouring halide atoms in olefin polymerisation has been demonstrated recently by Fujita et al. who used fluorinated phenoxyimine Ti catalysts,[43,44] but in the latter case the halide–alkyl interaction involves the β-H atom (and not the δ-H atom) and favors ethylene insertion. Thus the effect produced in the present study is different from that observed by Fujita and co-workers. We are aware that the proposed interpretation must be considered with care, in particular because our system is dynamic, and further investigations are needed for a better understanding of the observed phenomenon. As expected, when the low Ni concentration tests were repeated with larger amounts of MAO (runs 12,13), the activity of the catalytic system decreased.

Finally, we found that upon activation with MAO the nickel cyclopentadienyl complex **3** also dimerises ethylene (Table 2, entry 20). However, cyclopentadienyl substitution turned out to be more difficult, and accordingly somewhat lower activities were observed in this case.

Conclusion

The present study reveals the high degree of preorganisation of the large diphosphines **1** and **2**, which are well suited to forming nickel(II) chelate complexes. Activation with MAO of the corresponding [NiX$_2$(diphosphine)] complexes afforded ethylene dimerisation catalysts with remarkably high activities. A plausible explanation of the observed performance relies on a permanent and fast P-Ni-P bite angle variation taking place during the catalytic process and which incidentally may lower the transition state of the rate-determining step. This interpretation cannot be confirmed at the present stage but appears likely in view of the fanning motion which was shown to occur in **3** and taking also into account the lower activity of [NiBr$_2$(dppe)], a complex in which the bite angle of the diphosphine remains fixed near 90°. The observed catalytic activities are remarkable especially as ligands **1** and **2** are less basic than dppe, for which the reductive elimination step should intrinsically be favored. Regarding the second dynamics found in complex **3**, namely the oscillation about the Ni–P bonds, a possible driving force for this motion, but certainly not the only one, could arise from the cavity's marked tendency to fill the empty part of the hollow (nature abhors a vacuum) and hence to guest alternately the two *endo*-oriented PPh rings. Further work will concentrate on variants of **1** in which the inherent flexibility of the calixarene core is controlled. Overall, contrary to a general belief, the present work shows that *pseudo* bis(triphenylphosphine) ligands may result in high performance catalysts for ethylene dimerisation.

Experimental Section

General aspects: All reactions involving phosphines were performed in Schlenk flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. CDCl$_3$ was passed down a 5-cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^{1}H, ^{13}C, and ^{31}P were recorded with FT Bruker AV-300 or AV-500 spectrometer. ^{1}H NMR spectra were referenced to residual protonated solvent ($\delta = 7.26$ ppm for CDCl$_3$), ^{13}C chemical shifts are reported relative to deuterated solvent ($\delta = 77.0$ ppm for CDCl$_3$), and the ^{31}P data are given relative to external H$_3$PO$_4$. Gas chromatographic analyses were performed on a VARIAN 3900 gas chromatograph using a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 μm film thickness). The mass spectrum of **3** was recorded on a MSD Agilent spectrometer using CH$_2$Cl$_2$ as solvent; that of **5** was measured with a MicroTOF Bruker Daltonic spectrometer using CH$_3$CN as solvent. The molecular weight determination by vapour-pressure osmometry (CH$_2$Cl$_2$) of complex **4** was performed by Analytische Laboratorien, Lindlar, Germany. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur, Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. 5,17-Dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**1**),[26] 5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**2**)[26] and [{(η^5-C$_5$H$_5$)Ni(cod)}BF$_4$][45] were prepared according to methods reported in the literature. Anhydrous NiBr$_2$ was purchased from Aldrich and used as received. MAO 10 wt% (Aldrich) was used as a white powder which was obtained after evaporation of the solvent (60 °C, 3 h). This treatment reduces the amount of residual trimethylaluminium to about 3%. The resulting solid residue was dried over 3 h at 60 °C under vacuum. In the NMR data "C$_q$" denotes a quaternary carbon atom. The temperatures of the NMR experiments have been corrected, using methanol as reference. The accuracy is better than ±1 K.

Preparation of *cis-P,P'*-(η^5-cyclopentadienyl)-{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}nickel(II) tetrafluoroborate (3): To a solution of **1** (0.142 g, 0.127 mmol) in CH$_2$Cl$_2$ (20 mL) was added a solution of [(η^5-C$_5$H$_5$)Ni(cod)]BF$_4$ (0.038 g, 0.13 mmol) in CH$_2$Cl$_2$ (2 mL). After 3 h of vigorous stirring the solution was filtered through Celite and concentrated to about 5 mL. Addition of Et$_2$O afforded **3** (0.156 g, 92%) as a yellow precipitate; m.p. 270 °C. ^{1}H NMR (CDCl$_3$): $\delta = 7.19$–7.06 (m, 16H; PPh$_2$), 6.87 (br. s, 8H; *m*-H of OArP and PPh$_2$), 6.53 (br. s, 4H; *m*-H of OArBr), 5.03 (s, 5H; C$_5$H$_5$), 4.56 and 3.26 (2d, AB spin system, $^2J = 14.2$ Hz, 8H; ArCH_2Ar), 4.08 (t, $^3J = 8.1$ Hz, 4H; OCH$_2$), 3.83 (t, $^3J = 6.5$ Hz, 4H, OCH$_2$), 1.98–1.85 (m, 8H; OCH$_2$CH_2), 1.17 (t, $^3J = 7.3$ Hz, 6H; CH$_2$CH_3), 0.87 ppm (t, $^3J = 7.3$ Hz, 6H; CH$_2$CH_3); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 158.67$ and 157.24 (2 s; arom. C_q-O), 139.10–128.63 (arom. *C*'s), 115.69 (s; arom. C$_q$-Br), 97.35 (s; C$_5$H$_5$), 77.65 and 76.90 (2 s; OCH$_2$), 31.15 (s; ArCH$_2$Ar), 23.57 and 22.65 (2 s; CH$_2$CH$_3$), 10.82 and 9.60 (2 s; CH$_2$$CH_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, 300 K): $\delta = 31.0$ (s; PPh$_2$); elemental analysis (%) calcd for C$_{69}$H$_{69}$BBr$_2$F$_4$NiO$_4$P$_2$ ($M_r = 1329.58$): C 62.33, H 5.23; found: C 62.06, H 4.75; ES mass spectrum: *m/z* (%): 1241.3 (100) [$M-$BF$_4$]$^+$.

Preparation of *cis-P,P'*-dibromo-{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26, 27,28-tetrapropoxycalix[4]arene}nickel(II) (4): A mixture of **1** (0.524 g, 0.468 mmol) and anhydrous NiBr$_2$ (0.110 g, 0.502 mmol) in CH$_2$Cl$_2$ (50 mL) was stirred for 24 h at room temperature. The solvent was removed and the residue was taken up with CHCl$_3$. Addition of pentane afforded a green powder. The precipitate was filtered off, washed with cold pentane (3 × 10 mL) and then with diethyl ether (2 × 10 mL) and dried under vacuum to afford **4** (0.458 g, 73%) as a green solid; m.p. > 280 °C; elemental analysis (%) calcd for C$_{64}$H$_{64}$Br$_4$NiO$_4$P$_2$ ·0.25 CHCl$_3$ ($M_r = 1337.5 + 29.8$): C 56.44, H 4.74; found: C 56.16, H 4.91; molecular weight determination by osmometry (CH$_2$Cl$_2$): 1300 ± 65, corresponding to a monomer.

Preparation of *cis-P,P'*-dibromo-{5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}nickel(II) (5): A mixture of **2** (0.233 g, 0.242 mmol) and anhydrous NiBr$_2$ (0.053 g, 0.24 mmol) in CH$_2$Cl$_2$ (50 mL) was stirred for 24 h at room temperature. The solution was filtered through Celite. The solvent was evaporated and the residue was taken up with CHCl$_3$. Addition of pentane afforded a light green powder. The precipitate was filtered off, washed with cold pentane (3 × 10 mL) and then with diethyl ether (2 × 10 mL) and dried under vacuum to afford **5** (0.201 g, 70%) as a green solid; m.p. 263–266 °C (decomp); elemental analysis (%) calcd for C$_{64}$H$_{66}$Br$_2$NiO$_4$P$_2$·CHCl$_3$·C$_4$H$_{10}$O ($M_r = 1179.6 + 193.5$): C 60.35, H 5.65; found: C 60.74, H 5.77; MS (MALDI TOF): *m/z* (%): 1099 (20) [($M-$Br)$^+$, expected isotopic profile], 1018 (10) [($M-2$Br)$^+$, expected isotopic profile].

General catalytic testing procedure for ethylene dimerisation: A 100-mL steel autoclave was heated at 100 °C under vacuum for 2 h, cooled to room temperature and back-filled with ethylene. A solution of catalyst (4.5 μmol) in toluene (12 mL) was introduced into the autoclave by using a syringe under low ethylene pressure and stirred for 15 min. The reactor was vented upon which a solution of MAO (0.089 g, ca. 1.80 mmol) in toluene (10 mL) was added. The reactor was then pressurised. Two types of run were carried out (Table 2), those with an initial temperature of 25 °C, the temperature increase being, when necessary, controlled with an ice bath, and those in which the initial temperature was 40 °C. In the latter runs, no temperature regulation was applied. At the end of the run, the autoclave was cooled down to 7 °C and depressurised over 1 h. The flask containing the reaction mixture was weighed. This procedure was performed as quickly as possible to minimise the potential evolution of the butenes products. The reaction yield was determined from the final mass of reaction mixture versus the mass of the control reaction solution. To determine the mass of the control reaction solution (reaction mixture with no catalyst or co-catalyst), toluene (22 mL) was added to the autoclave and stirred under the same pressure at 25 °C for 30 min. The reactor was vented to ambient pressure and the flask containing the reaction mixture was weighed. The products were analysed by ^{1}H NMR spectroscopy and GC. 1-Butene was identified by ^{1}H NMR resonances at $\delta = 2.00$, 4.95 and 5.78 ppm. Resonances for the 2-butenes appear at $\delta = 1.54$ and 5.37 (*cis* form) and at $\delta = 1.58$ and 5.55 (*trans*) ppm.

Homopolymerisation of norbornene using 4: A solution of pre-catalyst **4** (0.006 g, 4.5 mmol) and norbornene (0.648 g, 6.7 mmol) in chlorobenzene (13 mL) was introduced by using a syringe into a Schlenk flask containing solid MAO (0.022 g, 0.45 mmol). The mixture was then vigorously stirred for 5 min. At the end of the test, acidified ethanol (20 mL) was added. The polymer was taken up in chlorobenzene, then precipitated with ethanol and dried under vacuum at 50°C overnight. Yield: 0.150 g (23.6%; TOF: 4261 h^{-1}). Under silmilar conditions [$NiBr_2$(dppe)] afforded a yield about tenfold lower.[46]

Crystallography: Single crystals of **3** were grown as pale orange plates by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature. Data were collected at 150 K on a Nonius Kappa CCD diffractometer using an $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. Formula: $C_{69}H_{70}BBr_2F_4NiO_4P_2\cdot 1/2\,CH_2Cl_2$; $M_r = 1371.98\ \mathrm{g\,mol^{-1}}$; monoclinic; space group *Cc* ; $a = 32.531(1)$, $b = 23.840(1)$, $c = 22.531(1)$ Å, $\beta = 133.711(1)°$, $V = 12630.6(9)$ Å^3; $Z = 8$; $\rho = 1.443\ \mathrm{g\,cm^{-3}}$; $\mu = 1.726\ \mathrm{cm^{-1}}$; $F(000) = 5640$. Crystal dimensions $0.22 \times 0.20 \times 0.06$ mm. Total reflections collected 35403, 16648 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.049; $R(I > 2\sigma(I)) = 0.0459$, $wR2 = 0.1169$ (all data), 1557 parameters; maximum/minimum residual density $0.942(0.072)/-0.579(0.072)\ \mathrm{e\,Å^{-3}}$. The crystal structure was solved in SIR 97[47] and refined in SHELXL97[48] by full-matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. The unit cell contains two distinctive isomers co-crystallising with a molecule of CH_2Cl_2. Figure 1 was drawn using PLATON.[49]

CCDC-237221 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Acknowledgment

We thank Mr. A. Rameau for analytical work and Dr. Y. Frère for providing us with technical facilities. We are grateful to the Université Louis Pasteur for support and thank the Ministère de L'Education Nationale for a research grant to M.L.

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Received: May 18, 2004