

Fast Propene Dimerization Using Upper Rim-Diphosphinated Calix[4]arenes as Chelators

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Abstract: The complexes $[\text{NiBr}_2 \cdot \mathbf{1}]$ and $[\text{NiBr}_2 \cdot \mathbf{2}]$, containing the upper rim-diphosphinated calixarenes 5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**1**) and 5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**2**) were assessed as propene dimerization catalysts. Combined with methylaluminoxane, both complexes result in highly efficient dimerization catalysts displaying C_6 selectivities in the range 80–97% and activities that compare with the best reported systems, the latter using PCy_3 as ligand. The origin of the re-

markable activities of the calixarene derivatives may be the ability of the diphosphine to undergo a periodic bite angle increase that incidentally favors the insertion step. Calixarenes such as **1** or **2**, which each incorporate two “stable” Ph_2PAr moieties, constitute interesting alternatives to the use PCy_3 in propene dimerization.

Keywords: calixarenes; homogeneous catalysis; ligand design; nickel; P ligands; propene dimerization

Introduction

Propene dimerization is an industrial reaction producing valuable compounds which find applications as gasoline additives and as precursors to various pharmaceuticals, agricultural chemicals, perfumes and polymers.^[1] All current applications involve nickel catalysis. In, for example, the Dimersol process, which is based on a Ni/Al system in the absence of any ligand, the non-regioselective propene dimerization affords C_6 -olefins with a composition of 22% *n*-hexenes, 72% 2-methylpentenes, and 6% 2,3-dimethylbutenes.^[2,3] The dimer selectivity is 80%, some trimers (18%) and tetramers (2%) also being formed. In contrast, regioselective dimerization occurs in the Sumitomo Chemical process, where a nickel salt is combined with tricyclohexylphosphine.^[4] In this case, 2,3-dimethylbutenes represent 85% of the dimers formed, the dimer selectivity being 59%. In fact, as already established by several studies, the product distribution in propene dimerizations catalyzed by Ni-phosphine complexes is strongly dependent upon the nature of the phosphine used.^[4,5] Thus, employing monophosphines that are both basic and bulky results in the high-

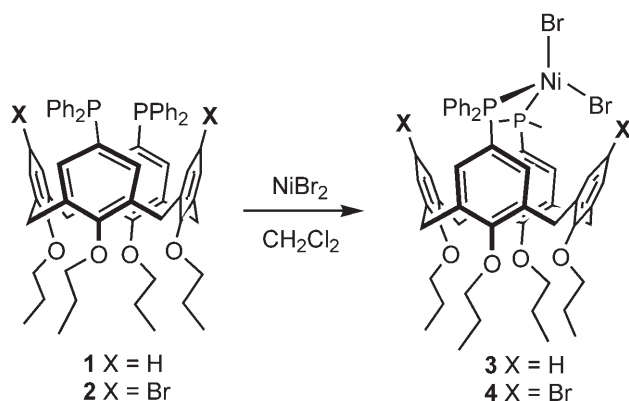
est activities. For example, on replacing PPh_3 by PCy_3 , the activity of Ni/ AlEt_2Cl systems is doubled, while the 2,3-dimethylbutene/ C_6 -olefins ratio increases from 14.6% to 83.1%.

As part of a program aimed at assessing the catalytic properties of the distally, upper rim-diphosphinated calix[4]arenes **1** and **2**, we now report a study on their use in the nickel-catalyzed dimerization of propene. In two previous reports we have shown that nickel(II) complexes containing these ligands constitute readily accessible precursors to highly active catalysts for some C–C coupling reactions.^[6,7] A major advantage of these catalysts, when compared with other active systems, is that the diphosphines are considerably less basic (and accordingly less sensitive) than those usually employed for reaching the same activities. In the present study, we also report the solid state structure of one of the precatalysts tested, namely the tetrahedral complex $[\text{NiBr}_2 \cdot \mathbf{1}]$. It is worth mentioning that to date chelating diphosphines have been very rarely employed in propene dimerization, most studies having focused on monophosphine ligands.^[8–11]

Results and Discussion

The two paramagnetic nickel(II) complexes used in this study, **3** and **4**, were prepared according to a method described previously (Scheme 1).^[6] The molecular structure of **3** was determined by a single crystal X-ray diffraction study. Important bond lengths and angles are given in Table 1. In the solid state (Figure 1), the nickel atom is positioned to one side, at a distance of 1.1 Å from the calixarene axis and, in keeping with the paramagnetic nature of this complex, adopts a tetrahedral geometry, with PNiP and BrNiBr angles of 110.4(1)° and 126.15(7)°, respectively. The latter two values are very close to those found in [NiBr₂(PPh₃)₂].^[12]

The calixarene unit adopts a flattened cone conformation; the interplanar angle between the phosphorus-bearing phenol rings is 18.5°, while that between the other two facing phenol rings is −108°. Apparently as a result of steric interactions with the calixarene framework, the two phosphino groups do not occupy equivalent positions in the structure. Thus, a single phenyl ring fills the



Scheme 1.

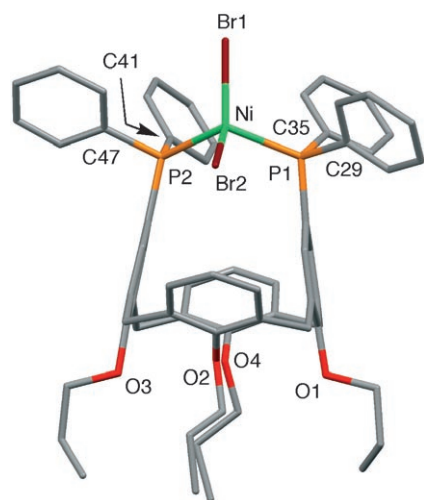


Figure 1. Molecular structure of complex **3**.

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

Distances			
Ni(1)–P(1)	2.339(3)	Ni(1)–P(2)	2.322(3)
P(1)–C(23)	1.819(9)	P(2)–C(47)	1.815(11)
P(1)–C(35)	1.842(10)	P(2)–C(11)	1.804(10)
P(1)–C(29)	1.847(10)	P(2)–C(41)	1.817(10)
O(1)–O(2)	5.66(1)	O(3)–O(4)	3.36(1)
Angles			
P(1)–Ni(1)–P(2)	110.43(10)	Br(1)–Ni(1)–Br(2)	126.15(7)
C(35)–P(1)–C(23)	105.3(5)	C(47)–P(2)–C(11)	104.1(5)
C(29)–P(1)–C(23)	102.1(5)	C(41)–P(2)–C(11)	106.7(5)
C(41)–P(2)–Ni	109.7(3)	C(35)–P(1)–Ni	119.7(4)

cavity entrance, and there is no symmetry to the structure. Its asymmetry is best seen by comparing the two angles C(41)–P(2)–Ni, 109.7°, and C(35)–P(1)–Ni, 119.7°. Similar distortions were observed in other chelate complexes obtained from **2**. The present study, which constitutes the first X-ray structural determination on a tetrahedral chelate complex obtained from **1**, firmly establishes that diphosphine **1** may undergo important bite angle variations. In the previously reported diamagnetic, square planar complexes with this and related diphosphines, smaller bite angles were observed, all lying in the range 99.7°–103.3°. It should be mentioned here that the latter complexes are dynamic in solution, the PMP plane undergoing a fast fanning motion which shifts the metal from one side of the calixarene axis to the other, the bite angle increasing by about 20° during this motion, as inferred from molecular mechanics calculations. This motion is compatible with the intrinsic flexibility of the calix[4]arene core.^[13,14] Given the bite angle in the tetrahedral complex **3**, 110.4°, it appears very likely that a similar motion may occur for this complex in solution, although we have no formal proof for this assumption.

The complexes **3** and **4** were tested in propene dimerization under constant pressure using 400 equivs. methylaluminumoxane (MAO) as activator (Table 2 and Table 3). Addition of MAO was accompanied by an instant color change (green to pale yellow), and no induction period was observed once MAO had been added. It turned out that operating in chlorobenzene afforded significantly higher activities than with toluene (Table 2, entries 1 and 2). Therefore, the runs were carried out systematically in this polar solvent.

Activity of the Catalysts

For both complexes, the turnover frequency increased with the propene pressure in the range 1–5 bar, the C₆-selectivity considerably surpassing 80% in most experiments. In a typical example, applying a propene

Table 2. Propene dimerization using **3**.^[a]

Run	<i>P</i> (C ₃ H ₆) [bar]	<i>V</i> (solv.) [mL]	Time [h]	<i>T</i> _{init} [°C]	Ni [μmol]	TOF ^[b] /10 ⁻⁵	<i>C</i> ₆ [wt %]	Product distribution [mol %] ^[c]					
								4M1P	4M2P	2M1P	2M2P	hex	TMEN
1 ^[d]	5	30	0.25	25	4.5	0.57	89.2	18.1	29.7	30.9	12.5	8.3	0.5
2	5	30	0.25	25	4.5	2.19	79.9	2.7	31.0	21.7	33.9	8.1	2.4
3	5	30	0.5	25	4.5	1.61	86.6	1.7	31.3	23.9	34.5	6.6	2.2
4	5	30	1	25	4.5	1.08	81.2	5.3	28.1	19.2	36.2	8.1	3.2
5	5	30	0.25	5	4.5	1.56	87.7	2.8	31.0	24.7	31.9	8.3	1.3
6	3	30	0.25	25	4.5	1.13	87.3	3.1	32.6	26.2	28.9	7.7	1.5
7	1	30	0.25	25	4.5	0.46	93.9	10.8	36.1	19.8	18.7	14.0	0.6
8	5	50	0.25	25	0.848	0.20	97.1	30.5	28.0	21.1	11.0	9.0	0.5
9 ^[e, f]	5	50	0.25	25	0.848	7.62	90.6	6.0	35.0	15.2	36.6	6.2	0.9
10 ^[f, g]	5	50	0.25	25	0.225	12.11	93.8	8.8	36.7	9.3	40.0	4.8	0.5
11 ^[f, h]	5	50	0.25	25	0.090	19.28	95.1	9.9	38.1	9.2	35.5	7.0	0.4
12 ^[h]	5	50	0.50	25	0.090	14.98	93.7	6.1	38.2	9.7	42.5	3.1	0.4
13 ^[f, h]	5	50	1	25	0.090	14.01	94.3	6.6	39.4	8.3	41.0	4.3	0.5

^[a] PhCl, MAO 400 equivs./Ni (MAO amount: 89 mg), yield determined by GC calibrated on heptane.^[b] mol (C₃H₆) mol⁻¹ (Ni) h⁻¹.^[c] 4M1P = 4-methyl-1-pentene, 4M2P = 4-methyl-2-pentene, 2M1P = 2-methyl-1-pentene, 2M2P = 2-methyl-2-pentene, hex = hexenes, TMEN = 2,3-dimethyl-2-butene.^[d] Toluene.^[e] MAO 2100 equivs./Ni (MAO amount: 89 mg).^[f] For these experiments the results were averaged.^[g] MAO 7900 equivs./Ni (MAO amount 89 mg).^[h] MAO 19800 equivs./Ni (MAO amount: 89 mg).**Table 3.** Propene dimerization using **4**.^[a]

Run	<i>P</i> (C ₃ H ₆) [bar]	<i>V</i> (solv.) [mL]	Time [h]	<i>T</i> _{init} [°C]	Ni [μmol]	TOF ^[b] /10 ⁻⁵	<i>C</i> ₆ [wt %]	Product distribution [mol %] ^[c]					
								4M1P	4M2P	2M1P	2M2P	hex	TMEN
1	5	30	0.25	25	4.5	2.37	86.5	1.8	31.7	19.3	31.6	13.9	1.8
2	5	30	0.25	15	4.5	2.63	84.8	2.6	30.1	21.9	35.9	7.4	2.1
3	5	30	0.25	5	4.5	2.59	90.7	1.4	32.6	20.1	27.7	17.2	1.1
4	5	30	0.25	-5	4.5	0.98	94.8	10.8	32.4	23.6	24.2	8.6	0.5
5	5	30	0.25	-15	4.5	0.36	96.8	24.2	29.0	20.2	16.5	9.7	0.3
6	3	30	0.25	5	4.5	1.20	91.5	5.6	33.1	22.7	30.4	7.3	0.8
7	1	30	0.25	5	4.5	0.80	92.2	2.7	30.1	30.5	30.0	5.7	1.0
8 ^d	5	50	0.25	25	0.09	25.99	94.9	6.8	36.8	12.3	39.2	4.6	0.4
9 ^d	5	50	0.50	25	0.09	17.82	95.0	8.1	39.7	7.4	40.1	4.2	0.4
10 ^d	5	50	1	25	0.09	13.49	94.3	9.2	37.0	9.5	39.9	3.8	0.5

^[a] PhCl, MAO 400 equivs./Ni (MAO amount: 89 mg), yield determined by GC calibrated on heptane.^[b] mol (C₃H₆) mol⁻¹ (Ni) h⁻¹.^[c] 4M1P = 4-methyl-1-pentene, 4M2P = 4-methyl-2-pentene, 2M1P = 2-methyl-1-pentene, 2M2P = 2-methyl-2-pentene, hex = hexenes, TMEN = 2,3-dimethyl-2-butene.^[d] MAO 19800 equivs./Ni (MAO amount: 89 mg); for these experiments the results were averaged.

pressure of 5 bar for 15 min to a solution of 4.5 μmol **4** in 30 mL PhCl at 25 °C, resulted in an activity of 2.4×10^5 mol (C₃H₆) mol⁻¹ (Ni) h⁻¹ with a *C*₆-selectivity of 86% (!) (Table 3, entry 1). This activity is *ca.* 2–3 times higher than that for other arylphosphine complexes, e.g., [NiBr₂(PPh₃)₂] or [NiBr₂(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂), when used under similar conditions (Table 4, entries 1–3). For comparison, the activity of the fastest dimerization catalyst reported to date, [NiCl₂(PCy₃)₂], is 2.8×10^5 mol (C₃H₆) mol⁻¹ (Ni) h⁻¹. However, with

the latter, the *C*₆-selectivity drops to 29.5% under the conditions defined above (Table 4, entry 5). Note that the TOF of the reactions carried out with **3** or **4** can be drastically increased by lowering the catalyst concentration. This is not surprising, since operating at a lower Ni/propene ratio results in a lower concentration of produced dimers, which may compete with propene for coordination and so hinder the dimerization reaction. For example, when the reaction described above for **4** was repeated with a catalyst concentration of 0.09 μmol/

Table 4. Propene dimerization using conventional nickel-phosphine complexes.^[a]

Entry	Ni complex	T_{init} [°C]	TOF ^[b] /10 ⁻⁵	C_6 [wgt %]	Product distribution [mol %] ^[c]					
					4M1P	4M2P	2M1P	2M2P	hex	TMEN
1	(dppe)NiBr ₂	25	1.15	87.0	2.2	35.8	14.8	41.0	5.0	1.2
2	(PPh ₃) ₂ NiBr ₂	25	0.80	91.9	7.9	29.3	31.5	20.5	10.0	0.8
3	(PPh ₃) ₂ NiBr ₂ ^[d]	25	0.72	86.0	11.1	29.0	35.1	13.1	10.9	0.8
4	(PPh ₃) ₂ NiBr ₂ ^[e]	25	0.09	95.8	17.6	29.7	23.7	14.0	14.6	0.4
5	(PCy ₃) ₂ NiCl ₂	25	2.82	29.5	1.3	53.0	27.6	13.3	1.6	3.2

^[a] PhCl 30 mL, $P(\text{C}_3\text{H}_6)=5$ bar, reaction time = 0.25 h, amount of Ni complex = 4.5 μmol except for entry 4 (0.848 μmol), MAO 400 equivs./Ni, yield determined by GC calibrated on heptane.

^[b] mol (C_3H_6) mol⁻¹ (Ni) h⁻¹.

^[c] 4M1P = 4-methyl-1-pentene, 4M2P = 4-methyl-2-pentene, 2M1P = 2-methyl-1-pentene, 2M2P = 2-methyl-2-pentene, hex = hexenes, TMEN = 2,3-dimethyl-2-butene.

^[d] Toluene 30 mL.

^[e] Using 0.848 μmol Ni and MAO 400 equivs./Ni, PhCl 50 mL.

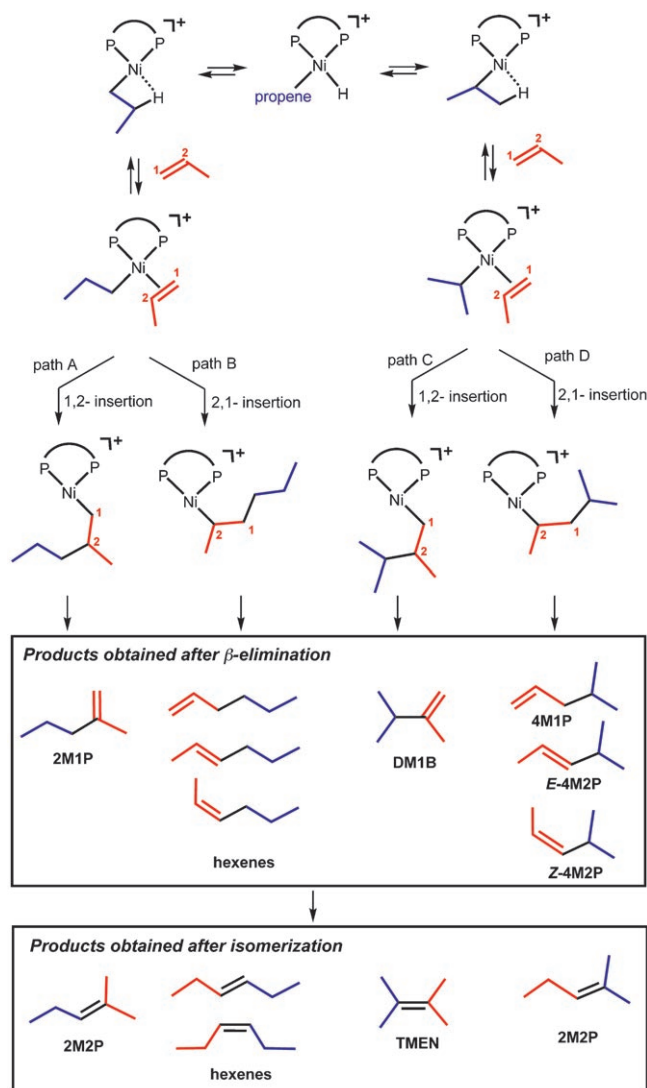
50 mL, the activity increased to 26×10^5 mol (C_3H_6) mol⁻¹ (Ni) h⁻¹ (Table 3, entry 8).

Interestingly, the activity of complex **4** is about 10–20% higher than that of complex **3**, whatever the catalyst concentration (compare, e. g., Table 2, entry 11 and Table 3, entry 8). This suggests that under the experimental conditions used the phenyl group Br atoms of ligand **2** may assist the catalytic process. The question whether weak $\text{CH} \cdots \text{Br}$ interactions may favor either the insertion step in the $[\text{Ni}(\text{diphos})(\text{propene})(\text{propyl})]^+$ intermediate or β -elimination at the end of the catalytic cycle cannot be answered at this stage. Further investigations such as, for example, substitution of the Br by F atoms, are needed to fully understand this phenomenon.^[15]

Finally, we observed that both catalysts remain active after 1 h, whatever their concentration (Table 2 entries 2–4 and 11–13, and Table 3, entries 8–10), the C_6 -selectivity being practically the same as for short time runs.

Product Distribution

The primary products as well as all isomerization products that were formed during propene dimerization are shown in Scheme 2, together with the possible pathways producing them.^[16] The product distributions are shown in the Tables 1 and 2. Both catalysts gave high methylpentene (MP) selectivities, this feature being slightly more pronounced at lower nickel concentrations. For example, with catalyst **4** ($P=5$ bar), MP selectivities higher than 95% were reached using a catalyst concentration of 0.09 $\mu\text{mol}/50$ mL PhCl (Table 3, entries 8–10), vs. 85% at a nickel concentration of 4.5 $\mu\text{mol}/30$ mL (Table 3, entry 1). As expected, higher temperatures favor isomerization of the pentenes formed as primary products. This is best seen on examining the variation of the proportion of the 4M1P (Table 3, entries 1–5). Isomerization also increases when raising the pro-

**Scheme 2.** Nickel-catalyzed propene dimerization. Organometallic intermediates and products.

pene pressure. This is probably due to the exothermic nature of the reaction, so that with high reaction rates, the temperature of the reaction medium increases. Interestingly, we found that with complex **3** the proportion of 4M1P, which is an α -olefin, may reach *ca.* 30% (Table 2, entry 8), provided the temperature of the reaction medium was maintained below 30 °C. Under similar conditions $[\text{NiBr}_2(\text{PPh}_3)_2]$ gave only 18% 4M1P (Table 4, entry 4). The rather high proportion of 4M1P could arise from a steric effect in the alkyl-Ni intermediate obtained according to path D (Scheme 2). Molecular models indicate that there should be steric repulsions between the calixarene backbone and the Ni-C₆ chain leading to preferential β -elimination at the β -CH₃ rather than the *sec*-butyl group.

The results presented above show that the catalytic systems based on **3** and **4** efficiently catalyze the dimerization of propene. The observed activities are 2–3 times higher than those obtained with other arylphosphines and approach those of the most active Ni-phosphine precatalyst known, $[\text{NiCl}_2(\text{PCy}_3)_2]$. The superiority of the present catalysts over the $[\text{NiCl}_2(\text{PCy}_3)_2]/\text{MAO}$ system is their considerable higher C₆-selectivity, which reaches 80–97%. The remarkable activity of the two catalysts is consistent with the observations already made in ethylene dimerization.^[6] The origin of the efficiency has already been discussed in our previous work and its rationalization relies on the hypothesis that in the active species the nickel atom moves from one side of the calixarene axis to the other (Scheme 3). Note, from studies carried out with the diamagnetic complex $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]^+$, it was inferred that, at 15 °C, the frequency of the fanning motion is *ca.* 70 Hz. As shown by molecular mechanics calculations, during this motion the PMP bite angle increases, reaching a maximum value when the metal crosses the calixarene axis. While the angle between the two Ni–P bonds increases, that between the other two bonds shrinks. In

other terms, the two reaction partners of the $[\text{Ni}(\text{diphos})(\text{propyl})(\text{propene})]^+$ intermediate (in which the metal center is assumed to adopt a planar geometry^[15]) come closer together, hence favoring the insertion step.

Conclusion

Overall, the present work demonstrates that, in catalytic propene dimerization, sensitive basic monophosphines may efficiently be replaced by robust bis(triarylphosphines) built on a calixarene backbone. It also constitutes a further confirmation^[17–21] that chelate complexes containing diphosphines with unusual bite angles may effectively modify the outcome of C–C bond forming reactions. Further work is aimed at optimizing the systems described in this study. In this respect, we will focus on variants of **1** and **2** having bulky substituents tethered at the lower rim that may induce larger bite angles.

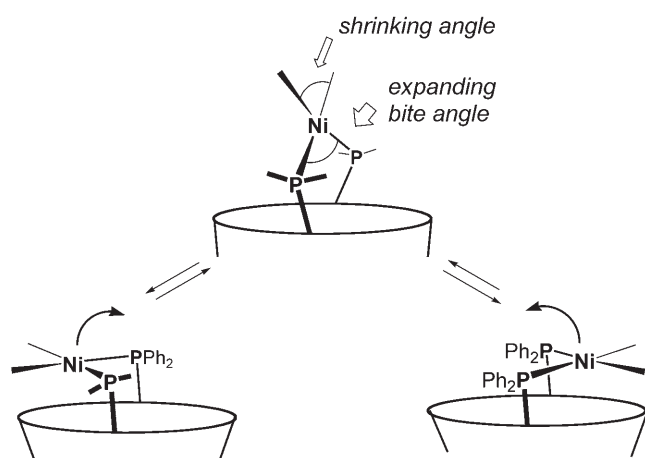
Experimental Section

General Remarks

All reactions involving nickel complexes were performed under dry argon. Solvents were dried by conventional methods and distilled immediately prior to use. 5,17-Bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**1**),^[22] 5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**2**),^[22] **3**,^[6] **4**,^[6] $[\text{NiBr}_2(\text{PPh}_3)_2]$ (**5**),^[12] $[\text{NiBr}_2(\text{dppe})]$ (**6**),^[23] and $[\text{NiCl}_2(\text{PCy}_3)_2]$ (**7**)^[24] were prepared according to methods reported in the literature. 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). MAO 10 wt % (Aldrich) was used as the white powder which was obtained after evaporation of the solvent (60 °C, 3 h). This treatment reduces the amount of residual trimethylaluminum to *ca.* 3%. The resulting solid residue was dried during 3 h at 60 °C under vacuum.

General Procedure for Propene Dimerization

A 200-mL Büchi glass autoclave was heated at 100 °C under vacuum for 2 h, cooled to room temperature and backfilled with propene. A solution of the precatalyst in a given solvent (20 mL) was introduced into the autoclave *via* a syringe under low propene pressure and stirred for 15 min. The reactor was vented, upon which a solution of MAO in the same solvent was added (see Tables 2–4 for details). The reactor was then pressurized. At the end of the run, the autoclave was cooled down to 5 °C and depressurized over 1 h. At this stage, only propene was evolved. 1 mL of heptane as internal standard was added and a sample of the reaction mixture was taken for GC analysis. The following GC conditions were applied: injector temperature: 250 °C; detector temperature: 275 °C; oven temperature program: 40 °C/10 min, 10 °C/min ramp, 220 °C/



Scheme 3. Proposed dynamics of the Ni-calixarene complexes.

5 min, 15 °C/min ramp, 250 °C/5 min. Retention times for the dimers are as follows: 4-methyl-1-pentene (4M1P), 1.65 min; 4-methyl-2-pentene (4M2P), 1.72 min; 2-methyl-1-pentene (2M1P), 1.81 min; 1-hexene, 1.82 min; 2-methyl-2-pentene (2M2P), 1.91 min; hexene isomers, 1.95 min; 2,3-dimethyl-2-butene (TMEN), 2.04 min. Peak identification was made with GC-MS.

Crystallography

Single crystals of **3** were grown as green plates by slow diffusion of heptane into a chloroform solution of the complex at room temperature. Data were collected at 120 K on a Nonius Kappa CCD diffractometer using an MoK α X-ray source ($\lambda = 0.71073$ Å) and a graphite monochromator. Formula: C₆₄H₆₆Br₂NiO₄P₂; $M_r = 1179.64$ g·mol⁻¹; monoclinic, space group $P2_1/c$, $a = 19.2276(4)$, $b = 15.5620(4)$, $c = 19.7108(5)$ Å, $\beta = 104.362(1)^\circ$, $V = 5713.5(2)$ Å³; $Z = 4$; $D_x = 1.371$ Mg·m⁻³, $\mu = 18.41$ cm⁻¹; $F(000) = 2440$. Crystal dimensions $0.40 \times 0.35 \times 0.22$ mm. 10045 independent reflections, 8211 with $I > 2\sigma(I)$. Goodness of fit on $F^2 = 1.198$; $R(I > 2\sigma(I)) = 0.095$; $wR2 = 0.28$, 659 parameters; maximum/minimum residual density $1.755/-0.991$ e Å⁻³. The crystal structure was solved with SIR97^[25] and refined with SHELXL97^[26] by full matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. After anisotropic refinement, many hydrogen atoms could be localized with a Fourier difference. CCDC-264585 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 Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Fax: (+44)-1223-336-033; or deposit@ccdc.cam.ac.uk].

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References and Notes

- [1] S. Muthukumar Pillai, M. Ravindranathan, S. Sivaram, *Chem. Rev.* **1986**, *86*, 353–399.
- [2] D. Commereuc, Y. Chauvin, G. Léger, J. Gaillard, *Rev. Inst. Fr. Pet.* **1982**, *37*, 639–649.
- [3] M. E. Bluhm, C. Folli, D. Pufky, M. Kröger, O. Walter, M. Döring, *Organometallics* **2005**, *24*, 4139–4152.
- [4] M. Itagaki, G. Suzukamo, K. Nomura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 79–82.
- [5] B. Bogdanovic, B. Spliethoff, G. Wilke, *Angew. Chem. Int. Ed.* **1980**, *19*, 622–623.
- [6] M. Lejeune, D. Sémeril, C. Jeunesse, D. Matt, F. Perruch, P. J. Lutz, L. Ricard, *Chem. Eur. J.* **2004**, *10*, 5354–3360.
- [7] D. Sémeril, M. Lejeune, C. Jeunesse, D. Matt, *J. Mol. Catal. A: Chemical* **2005**, *239*, 257–262.
- [8] G. G. Eberhardt, *U. S. Patent* 3,482,001, **1969**; *Chem. Abstr.* **1970**, *72*, 42720.
- [9] T. Hata, K. Takahashi, A. Miyake, *Japanese Patent* 47022807, **1972**; *Chem. Abstr.* **1972**, *77*, 87812.
- [10] H. E. Dunn, *U. S. Patent* 3,636,128, **1972**; *Chem. Abstr.* **1972**, *76*, 71985.
- [11] K. J. Cavell, A. F. Masters, *Aust. J. Chem.* **1986**, *39*, 1129–1134.
- [12] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, *J. Chem. Soc. A* **1968**, 1473–1486.
- [13] E. Dahan, S. E. Biali, *J. Org. Chem.* **1991**, *56*, 7269–7274.
- [14] V. Böhmer, *Angew. Chem. Int. Ed.* **1995**, *34*, 713–745.
- [15] NMR measurements carried out on **3**/MAO/hexene mixtures (in C₆D₆) revealed only the presence of diamagnetic species. Hence, it appears likely that during catalysis the nickel atom adopts a *planar* geometry. We assume that in the catalytic intermediates obtained from **4**, the nickel centre has also this coordination geometry. Molecular models show that in the latter, the two Br atoms of the calix platform do not sterically interact with the metal plane.
- [16] S. A. Svejda, M. Brookhart, *Organometallics* **1999**, *18*, 65–74.
- [17] M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, W. Keim, *Chem. Commun.* **1995**, 2177–2178.
- [18] M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.* **1998**, 155–157.
- [19] P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895–904.
- [20] J. N. L. Dennett, A. L. Gillon, K. Heslop, D. J. Hyett, J. S. Fleming, C. E. Lloyd-Jones, A. G. Orpen, P. G. Pringle, D. F. Wass, J. N. Scutt, R. H. Weatherhead, *Organometallics* **2004**, *23*, 6077–6079.
- [21] I. Albers, E. Álvarez, J. Cámpora, C. M. Maya, P. Palma, L. J. Sánchez, E. Passaglia, *J. Organometal. Chem.* **2004**, *689*, 833–839.
- [22] M. Lejeune, C. Jeunesse, D. Matt, N. Kyritsakas, R. Welter, J.-P. Kintzinger, *J. Chem. Soc. Dalton Trans.* **2002**, 1642–1650.
- [23] C. A. McAuliffe, D. W. Meek, *Inorg. Chem.* **1969**, *8*, 904–907.
- [24] P. Stone, Z. Dori, *Inorg. Chim. Acta* **1971**, *5*, 434–438.
- [25] A. Altomare, M. C. Burla, M. Camalli, G. Casciarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data*.
- [26] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, **1997**.