Coordination Chemistry of Large Diphosphanes − Directional Properties of a Calix[4]arene Proximally Substituted by Two $-OCH_2PPh_2$ Podand Arms

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Dedicated to Professor Jean-Pierre Sauvage on the occasion of his 60th birthday

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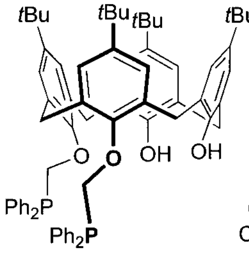
The proximally-functionalised calixarene 5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene (**1**), a large diphosphane in which the P^{III} centres are separated by 10 bonds, behaves as a chelating ligand towards NiX_2 moieties (X = Cl, Br). As shown by three X-ray studies carried out on complexes of the type [NiX_2·**1**], the diphosphane is able to accommodate either tetrahedral or strongly distorted tetrahedral coordination geometries, but not a square planar one. In all structures, the ligand positions the nickel atom away from the calixarene axis. In the presence of methylaluminoxane (MAO), [$NiCl_2$·**1**] effectively catalyses the oligomerisation of ethylene, affording C_4–C_{12} oligomers.

Introduction

Calix[4]arenes locked in the cone conformation are remarkable building blocks for the preparation of multifunctional ligands.[1−5] They are frequently used as preorganising platforms allowing control of the orientation of podands anchored to one of the rims and hence for imposing a particular coordination geometry upon a complexed metal ion.[6,7] Depending upon their nature, length and flexibility, convergent binding sites tethered at the same rim may not only result in high complexation selectivities but also produce metal complexes with unconventional catalytic properties.[8−18] In a recent paper, we reported the coordination chemistry of the diphosphane **1** and have shown that this conical calixarene,[19] as well as some derivatives,[20,21] forms square planar Pt^{II} chelate complexes (**A**) exclusively in the *cis* configuration in which the P-M vectors are oriented away from the calixarene axis, thus positioning the metal outside the conical domain defined by the macrocycle. The ligand bite angle in *cis*-[$PtCl_2$·**1**], as revealed by an X-ray study, is 103.4(1)°. In order to further substantiate the directional properties of this diphosphane, we have now investigated its coordination behaviour towards $NiCl_2$ and $NiBr_2$ units, two versatile fragments known to form either tetrahedral or square planar [NiX_2(phosphane)$_2$] metal complexes. The present study describes the syntheses and structures of three paramagnetic nickel(II) complexes based on **1** and illustrates that the ligand bite angle may undergo major variation, hence enabling the metal centre to approach closer to the calixarene core.



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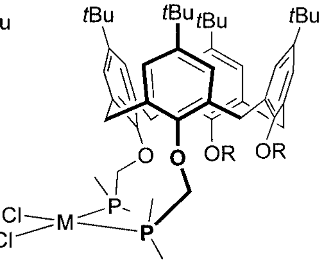

A

Results and Discussion

From our previous study it appears that despite its considerable length, diphosphane **1** is sufficiently preorganised to readily form chelate complexes with the $PtCl_2$ moiety.[19] Complexation of this fragment results in formation of a compound in which the platinum atom is oriented outwards from the cone defined by the calixarene. The same com-

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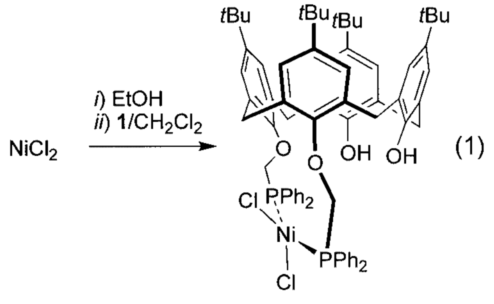
plexation behaviour towards $PtCl_2$ was observed when using analogues of **1** in which the phenol rings bear substituents.[19,21] Inverting the orientation of the P lone pairs is a challenging goal that would lead to complexes where the metal is brought closer to the calixarene axis, thus favouring interactions between the coordination centre and the bulky calixarene core. In order to study whether **1** gives access to such structures, we decided to investigate the coordination properties of **1** towards the nickel(II) centre which has a greater stereoflexibility than platinum(II).

The preparation of complex **2** required a two-step procedure consisting of (*i*) dissolution of anhydrous $NiCl_2$ in small amounts of EtOH to form an unidentified species which, unlike $NiCl_2$, is soluble in CH_2Cl_2 and (*ii*) treatment of the thus formed species with a solution of **1** in CH_2Cl_2 (Equation 1). A direct synthesis in CH_2Cl_2 was impossible due to the insolubility of $NiCl_2$ in this solvent, while attempted synthesis in pure EtOH did not result in phosphane coordination. We found that the best $EtOH/CH_2Cl_2$ ratio was ca. 1:10.



2

The dark blue complex **2** is paramagnetic and was characterised by elemental analysis and an X-ray diffraction study. Its molecular structure is shown in Figure 1. The shape of the calixarene core deviates only slightly from an ideal cone. Thus, the "centroid-centroid" separations between the distal phenol units are 6.45 and 6.93 Å, respectively, while the dihedral angles between the calixarene reference plane [defined as the mean plane of the bridging C atoms, here C(12), C(23), C(34), C(45)] and those of the four phenol rings are 115° (C2), 103° (C18), 134° (C29) and 124° (C40). Hydrogen bonds involving the hydroxy groups and the neighbouring phenolic oxygen atoms may contribute to this structure, as indicated by the rather short O(1)···O(3) [2.78(2) Å], O(2)···O(4) [2.87(2) Å] and O(3)···O(4) [2.67(2) Å] separations (cf. O(1)···O(2) 3.46(2) Å]. The compound crystallises with two dichloromethane molecules, one of them lying inside the calixarene basket. The shortest contacts of the latter with the aromatic walls are between H(71b) and C(27) (2.83 Å), and H(71b) and C(28) (2.84 Å). Note, considerably shorter contacts have been found in other calixarenes with CH_2Cl_2 guests.[22] The Ni atom is slightly bent towards the exterior of the cavity and its coordination geometry may be regarded as being between square planar and tetrahedral. By considering the PNiP and ClNiCl angles of 158.45(3)° and 158.29(4)°, one gets the impression that the ligand is attempting unsuccessfully to behave as a *trans* spanning ligand. Clearly, complexation results in a strained chelate ring, as shown by the C(1)P(1)Ni and C(46)P(2)Ni angles of 109.9(1)° and 108.1(1)°, respectively, which are about 10° smaller than the other CPNi angles. It should be remembered here that, as shown in previous studies, calix[4]arenes having at least two proximal $-OCH_2PPh_2$ units display a marked propensity to form *cis*-chelated structures, no *trans* complexes having been reported to date. The NiP bond lengths [2.220(1), 2.247(1) Å] lie in the range found for complexes of the general formula *trans*-$[NiCl_2(PPh_2R)_2]$.[23–25]

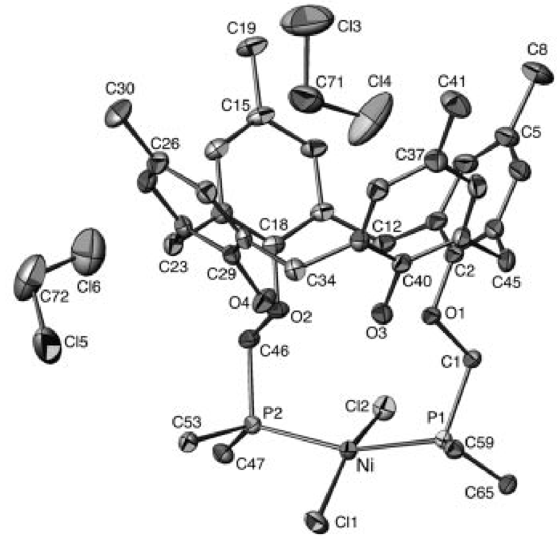
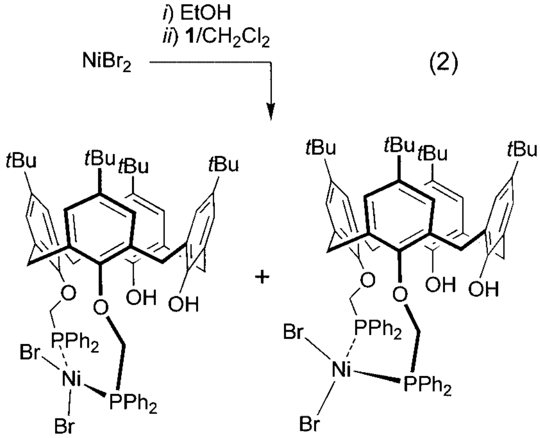


Figure 1. Molecular structure of the blue complex $[NiCl_2\cdot\mathbf{1}]\cdot 2CH_2Cl_2$ ($\mathbf{2}\cdot 2CH_2Cl_2$); only the C_{ipso} atoms of the P-phenyl rings are shown; the *t*Bu groups are not shown in full

Complexes **3** and **4** were obtained as a binary mixture, but could be separated mechanically after crystallisation. They were prepared similarly to the method outlined above for **2**, but starting from anhydrous $NiBr_2$ (Equation 2). Crystallisation from dichloromethane/heptane afforded a mixture of crystals of turquoise **3** and red-brown **4**.



3 **4**

Obtaining this crystal mixture is easily reproducible. It appears likely that both compounds exist in equilibrium in solution, since dissolving crystals of either of them afforded the same green solution (toluene or CH_2Cl_2). The two molecular structures were determined by single-crystal X-ray diffraction studies (Figure 2 and 3). Again, both calixarenes adopt the shape of a cone having a "circular" cross section and both cavities host a dichloromethane molecule. As found in **2**, hydrogen bonds involving the hydroxy groups appear to stabilise the whole calixarene geometry (Table 1). The coordination geometry of **3** is close to that found in **2**, as can be seen from the PNiP and BrNiBr angles of 158.58(3)° and 152.19(2)°, respectively. In contrast, **4** has a conventional tetrahedral stereochemistry with considerably smaller PNiP [118.6(3)°] and BrNiBr [138.55(5)°] angles. Incidentally, the metallomacrocyclic unit of **4** is less strained than those of **2** and **3**. For example, the values of the NiPC$_\alpha$ angles in this unit are 119.0(1)° and 117.6(1)°. We note that in all three complexes, the Ni atom is orientated away from the calixarene axis. In each structure, a halogen atom approaches the axial H(12) atom but weak interactions with this methylene H are likely to occur in **2** and **3** [$H_{axial}(12)\cdots X$ distances (Å): 2.77, 2.84 and 3.00, respectively, for **2**, **3** and **4**]. These weak interactions could explain why the Ni−X(2) bonds of **2** and **3** are slightly but significantly longer than the corresponding Ni−X(1) bonds. Involvement of $ArCH_{axial}$ hydrogen atoms in weak bonding have recently been found in other calixarenes, in particular in some agostic CH···M interactions.[21] Finally, it is noteworthy that there is no indication in the syntheses outlined above of oligomer formation, illustrating the high degree of preorganisation of calixarene **1**.

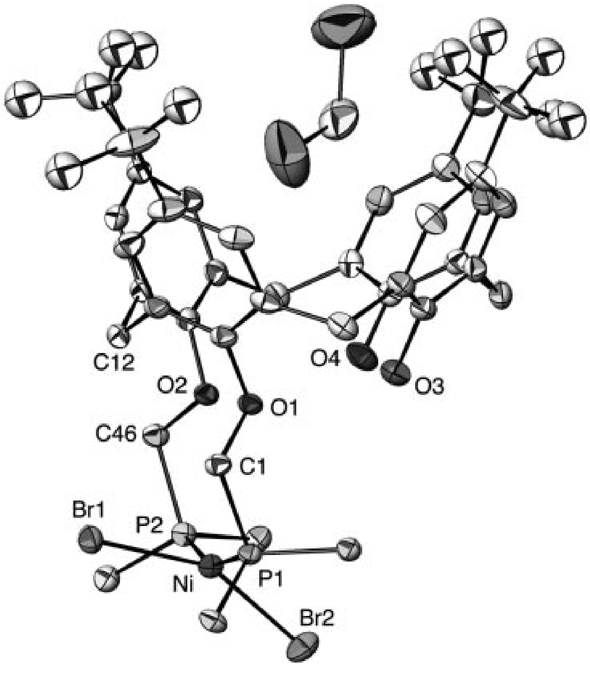


Figure 2. Molecular structure of the turquoise complex $[NiBr_2\cdot\mathbf{1}]\cdot 2CH_2Cl_2$ ($\mathbf{3}\cdot 2CH_2Cl_2$); for clarity, only the C_{ipso} atoms of the P-phenyl rings are shown; the *t*Bu groups are not shown in full

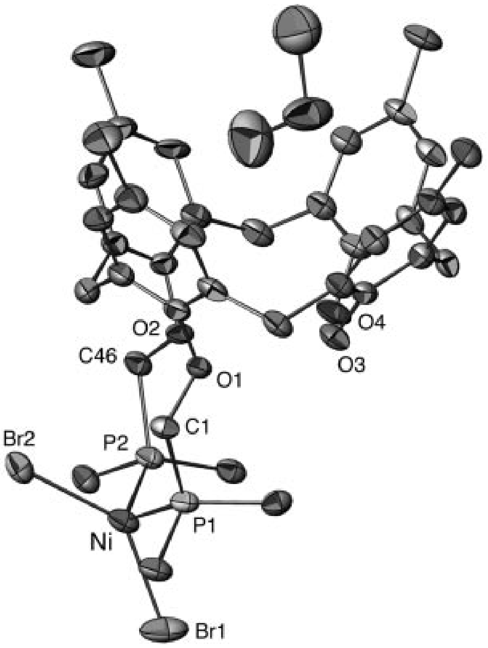


Figure 3. Molecular structure of the red brown complex $[NiBr_2\cdot\mathbf{1}]\cdot 1.75CH_2Cl_2$ ($\mathbf{4}\cdot 1.75CH_2Cl_2$); for clarity, only the C_{ipso} atoms of the P-phenyl rings are shown; the *t*Bu groups are not shown in full

Table 1. Relevant structural parameters for **2**, **3** and **4** in the solid state

	2	**3**	**4**
Distances (Å)			
O1···O2	3.46(2)	3.47(2)	3.30(2)
O1···O3	2.78(2)	2.78(2)	2.74(2)
O1···O4	3.96(2)	3.98(2)	4.11(2)
O2···O3	4.33(2)	4.33(2)	4.14(2)
O2···O4	2.87(2)	2.89(2)	3.05(2)
O3···O4	2.67(2)	2.68(2)	2.63(2)
Ni−P1	2.247(1)	2.235(1)	2.290(9)
Ni−P2	2.220(1)	2.215(1)	2.303(9)
Ni−X1	2.150(2)	2.286(1)	2.320(6)
Ni−X2	2.168(2)	2.308(1)	2.338(6)
Angles (°)			
PNiP	158.45(3)	158.58(3)	118.6(3)
XNiX	158.29(4)	152.19(2)	138.55(5)
Dihedral angles (°) between the phenol rings and the calixarene reference plane	**2**	**3**	**4**
(C2)	115(1)	115(1)	114(1)
(C18)	103(1)	104(1)	110(1)
(C29)	134(1)	136(1)	122(1)
(C40)	124(1)	124(1)	133(1)

It is well known that $[NiCl_2(phosphane)_2]$ complexes constitute good precatalysts for the oligomerisation or polymerisation of olefins, the outcome of the reaction being strongly dependent on the nature of the phosphane.[26,27] Thus for example, $[NiCl_2(PCy_3)_2]$ activated with $AlEt_2Cl$ becomes a highly selective ethylene dimerisation catalyst.[28] A typical activity for this complex is 1600 $mol(C_2H_4)\cdot mol(Ni)^{-1}\cdot h^{-1}$.[29] Other complexes, for instance

Table 2. Ethylene oligomerisation with **2** (conditions: complex **2** (6 μmol), MAO (0.500 g), toluene (20 mL), initial temperature 25 °C)

P(C_2H_4) (bar)	α (°)	TOF (mol C_2H_4)/(mol [Ni]·h)	Activity g C_2H_4/(mmol [Ni]·h·bar)	Olefin distribution (wt.-%)					
				C_4	C_6	C_8	C_{10}	C_{12}	C_{14}
10	0.18	3100	8.7	73.9	19.9	4.8	1.1	0.3	/
30	0.22	9800	9.1	68.4	22.6	6.6	1.8	0.5	0.1

[$NiBr_2${$Ar_2PN(Me)PAr_2$}] (Ar = *o*-*i*PrC_6H_4), display a high ethylene polymerisation activity [with activities as high as 79000 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1}] producing high molecular weight polymers.[30] Recent work on [$NiCl_2$(chelate)] complexes has clearly underlined that a subtle combination of backbone rigidity and partial steric protection of the nickel centre is the determining factor for product distribution control.[31,32] It is also worth mentioning that to date, long chain diphosphanes having a backbone containing more than six carbon atoms have not been studied in olefin oligomerisation/polymerisation systems.[27,33] Reports dealing with generic calix[4]arenes that were employed in olefin polymerisation have appeared in the literature, but these remain scarce.[34−37]

In view of the fact that ligand **1** possesses a flexible bite angle, we decided to assess the role of complex **2** in ethylene oligomerisation. The runs were performed in toluene ([catalyst] = 0.3 mmol/dm^3) using methylaluminoxane (MAO) (1500 equiv.) as the activator. Operating under an ethylene pressure of 10 bar and stopping the reaction after 1 h, produced C_4 to C_{12} oligomers. The observed activity was 3100 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1}. The product distribution is typically of the Schulz−Flory type, with α about 0.2 (Table 2).

Applying a pressure of 30 bar increased the activity up to 9800 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1} without modifying the product distribution. Interestingly, no catalyst deactivation was observed during these 1 h experiments. As shown by the study outlined above, diphosphane **1** is able to undergo large bite angle variations but this has only little impact on the catalyst activity. For comparison, in terms of activity and selectivity, the catalyst performance compares with that of [$NiCl_2(Ph_2PCH_2PPh_2)$], a complex in which the chelating unit is much more strained than that in **2**.[38] The structural studies revealed that, whatever the coordination geometry of nickel complexes containing **1**, the bulky calixarene core is remote from the nickel centre, resulting in a rather uncrowded metal environment and hence facilitating reductive elimination steps.

Conclusion

In this study we have shown that in the presence of NiX_2 moieties the large diphosphane **1** straightforwardly forms chelate complexes, thus confirming the good preorganisation of the ligand. While previous studies have shown that **1** and its congeners act exclusively as *cis*-chelators towards the $PtCl_2$ moiety, we have discovered that **1** is also able to adapt to various tetrahedral coordination geometries, some of them being extremely distorted. Thus, **1** gives access to bite angles lying in the range 103.4°−158.6°. The fact that to date no complex could be synthesised in which **1** behaves as a genuine *trans* chelator obviously arises from the rigidity of the spacer that links the P^{III} atoms as well as the shortness of the two phosphorus arms. The present work further demonstrates that ligand **1** is able to bring the metal centre closer to the calixarene axis than was previously observed in Pt^{II} complexes, although the PM vectors remain oriented outwards. Activation of **2** with MAO afforded a good ethylene oligomerisation catalyst resulting selectively in C_4−C_{12} oligomers. The formation of short oligomers suggests that during catalysis the nickel environment is slightly encumbered hence favouring reductive elimination over chain propagation. The formation of polymers could possibly be forced by orientating the PM vectors towards the calixarene axis so as to ensure partial protection of the metal. Further studies are aimed at exploiting the bite angle flexibility of diphosphane **1** in catalytic reactions.

Experimental Section

General Conditions: Solvents were dried with suitable reagents and freshly distilled under dry nitrogen before use. All reactions were carried out using modified Schlenk techniques under a dry nitrogen atmosphere. Elemental analyses were performed by the Service de Microanalyse, Centre de Recherche Chimie, Université Louis Pasteur, Strasbourg. 5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene (**1**) was prepared according to the previously reported method.[19] 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 ca. 3%.

Synthesis of Dichloro-{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene}nickel(II) (2): Anhydrous $NiCl_2$ (0.019 g, 0.15 mmol) was dissolved in hot ethanol (0.5 mL) whereupon a solution of **1** (0.153 g, 0.15 mmol) in CH_2Cl_2 (5 mL) was added. During addition the pale yellow solution turned deep blue. After 0.25 h, the solvent was removed in vacuo. The residue was treated with a small volume of pentane (5 mL) and the resultant suspension filtered through a glass frit. Cooling to −30 °C precipitated a dark blue powder which was dried in vacuo. Yield: 0.070 g, 40%. $C_{70}H_{78}Cl_2NiO_4P_2$ (M_r = 1174.93): calcd. C 71.56, H 6.69; found C 71.66, H 6.90. Single-crystals suitable for X-ray diffraction were obtained by slow diffusion at room temperature of hexane into a CH_2Cl_2 solution of the complex.

Table 3. Crystal and structure refinement data for **2**, **3** and **4**

Formula	$C_{70}H_{78}Cl_2NiO_4P_2{\cdot}2CH_2Cl_2$	$C_{70}H_{78}Br_2NiO_4P_2{\cdot}2CH_2Cl_2$	$C_{70}H_{78}Br_2NiO_4P_2{\cdot}1.75CH_2Cl_2$
Molecular mass	1344.73	1433.65	1387.97
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	12.7590(10)	12.736(5)	18.868(2)
b (Å)	16.7150(10)	16.895(5)	14.1060(10)
c (Å)	18.4130(10)	18.441(5)	29.853(3)
α (°)	110.11(5)	110.599(5)	90
β (°)	104.31(5)	104.026(5)	105.62(5)
γ (°)	100.36(5)	100.257(5)	90
V (Å^3)	3418(2)	3448.8(19)	7651.8(12)
Z	2	2	4
D(calcd.) (g·cm^{-3})	1.307	1.380	1.205
μ(Mo-K_α) (mm^{-1})	0.612	1.688	1.470
F(000)	1412	1484	2882
Crystal size (mm)	0.08 × 0.10 × 0.13	0.05 × 0.07 × 0.08	0.06 × 0.07 × 0.08
Temperature (K)	173	173	173
Radiation, λ (Mo-K_α) (Å)	0.71069	0.71069	0.71069
$\Theta_{\text{min.,max.}}$ (°)	1.3, 30.0	1.8, 30.0	1.0, 30.0
Data set (h; k; l)	−17/17; −23/22; 0/25	−17/17; −23/23; −25/24	−21/26; −19/19; −34/42
Total, unique data, R(int.)	19905, 19905, 0.035	41543, 20069, 0.050	36106, 20421, 0.073
Obsd. data with $I > 2.0\sigma(I)$	14740	15013	10790
$N_{\text{reflections}}$, $N_{\text{parameters}}$	19905, 766	20069, 766	20421, 748
$R1$, $wR2$, S	0.0712, 0.1863, 1.05	0.0663, 0.1496, 1.03	0.0989, 0.3089, 1.02
Min., max. residual electron density (e·Å^{-3})	−1.07, 1.17	−1.13, 1.29	−1.25, 1.56

Synthesis of Dibromo-{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene}nickel(II), Isomers 3 and 4: Anhydrous $NiBr_2$ (0.041 g, 0.19 mmol) was dissolved in hot ethanol (0.5 mL) resulting in a pale orange solution. A solution of **1** (0.200 g, 0.19 mmol) in CH_2Cl_2 (5 mL) was then added and the mixture turned green. After 0.25 h, the solution was evaporated to dryness. The residue was redissolved in CH_2Cl_2 (ca. 1 mL), whereupon pentane was added to precipitate a pale green powder which was recovered by filtration. Yield: 0.197 g, 82%. The green powder was then dissolved in CH_2Cl_2. Slow diffusion of heptane into the resultant intense green solution afforded crystals of **3** (turquoise colour) and **4** (red brown) which were separated mechanically. Elemental analyses were carried out on both isomers after drying in high vacuum: $C_{70}H_{78}Br_2NiO_4P_2$ (M_r = 1263.83): calcd. C 66.53, H 6.22; found for **3**: C 66.22; H 5.75; found for **4**: C 66.50; H 6.42.

Crystal Structure Determination of $2{\cdot}2CH_2Cl_2$: Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. Data were collected with a Nonius KappaCCD diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2.[39] Hydrogen atoms were located using the geometric method. The crystal data and structural refinement details are listed in Table 3. The compound was found to crystallise with two molecules of dichloromethane, one of them lying inside the cavity. CCDC-234357 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Structure Determination of $3{\cdot}2CH_2Cl_2$ and $4{\cdot}1.75CH_2Cl_2$: Single crystals of **3** and **4** were obtained simultaneously by slow diffusion of heptane into a solution of [$NiBr_2{\cdot}$**1**]. Data collection and structure solution were carried out as above for **2** (Table 3). The poorer quality of the structure of **4** is due to disordered solvent molecules, whether they lie inside or outside the cavity. CCDC-234358 (for **3**) and CCDC-234359 (for **4**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Oligomerisation of Ethylene: The catalytic runs were carried out in a 100 mL glass-lined stainless steel autoclave containing a magnetic stirring bar. In a typical run, a solution of complex **2** (0.007 g, 6 μmol) in toluene (15 mL) was introduced under nitrogen into the autoclave whereupon a solution of MAO (0.500 g) in toluene (5 mL) was added. After stirring for ca. 1 min the autoclave was pressurised with ethylene and the pressure (10 or 30 bar) was maintained at a constant value. During the runs described in this work, the temperature raised from 25 °C to 37 °C when operating at 10 bar and up to 42 °C under 30 bar. After 1 h, the autoclave was cooled to 7 °C and then depressurised over a period of 1 h. Heptane (200 μL), which serves as internal reference for the GC analysis, was then added to the reaction mixture. The liquid phase was analysed with a VARIAN 3900 gas chromatograph equipped with a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness).

Acknowledgments

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