ChemPubSoc Europe

DOI: 10.1002/ejic.201901074

EurJIC European Journal of Inorganic Chemistry

Full Paper

Molecular Containers

# Metallated Container Molecules: A Capsular Nickel Catalyst for Enhanced Butadiene Polymerisation

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**Abstract:** A unique, covalently constructed capsular catalyst obtained by reaction of [Ni($\eta^5$-$C_5H_5$)(1,5-cyclooctadiene)] $BF_4$ with the double-calixarene-derived diphosphine 1,3-bis(5-diphenylphosphino-25,26,27,28-tetrapropoxycalix[4]aren-17-yl)-benzene (**1**) has been shown to polymerise butadiene at a rate considerably superior to that of previously known catalysts. The reported results indicate that the container structure of the covalent complex is retained during catalysis.

## Introduction

The design and synthesis of new molecular catalysts constitutes a continuing, central theme of chemical research.[1] The conduct of metal-catalysed reactions in a confined environment, in particular, is an important example of a relatively new concept in homogeneous catalysis. Impressive contributions to this field have already been made by Nolte,[2] Rebek,[3] Raymond,[4] Fujita,[5] van Leeuwen,[6] Reek,[7] Tieffenbacher[8] and others,[9] who have highlighted the properties of deeply embedded catalytic systems, notably in terms of selectivity and efficiency, as well as their possible use in aqueous media.[10] To date research in this field has been dominated by a supramolecular approach relying on the utilisation of functional synthons, some of them metalated, which readily self-assemble and incidentally create a microenvironment able to incorporate an active site.[11] A major drawback of these systems lies in their rather labile nature, rendering them unfit for use in industrial applications. Confined covalent catalysts offering the advantage of structural robustness, a key property in catalysis, are relatively rare. This arises in part from the difficulty in synthesising container molecules with convergent donor atoms able to position a metal inside the cavity.[12] Here, we describe the development of covalent capsular systems immobilising catalytic nickel and palladium centres inside their cavity. The targeted metallo-capsules were obtained from double calixarene **1** and were designed so as to possess portals sufficiently large to formally allow entry of small substrates and subsequent escape of products formed inside the cavity. A concrete example of the catalytic potential of such complexes is provided by the use of a nickel capsule in butadiene polymerisation.

## Results and Discussion

Our strategy for creating metallo-capsules relied on the use of the long diphosphine **1**, a potential chelator incorporating two conical calix[4]arene subunits linked by a phenylene spacer. We anticipated that upon chelation of a metal centre with two free, *cis*-positioned binding sites, the diphosphine would not only adopt a rigid, capsular form, but also confine the coordinated metal centre inside the resulting container. Thus, capsular complex **2** was obtained *quantitatively* by reaction of [Ni($\eta^5$-$C_5H_5$)-(cod)]$BF_4$ (cod = 1,5-cyclooctadiene) with **1** (Scheme 1, top). The use of a cationic nickel reactant allowed for a fast binding process, thereby favouring chelate formation over that of oligomeric complexes, which often form with long diphosphines.[13] Complex formation was inferred from the mass spectrum, which shows a strong peak at *m/z* 1750.75 having exactly the isotopic profile expected for $[M - BF_4]^+$. Complex **2** has $C_s$ symmetry, consistent with chelation of the metal, as deduced from analysis of both the $^{31}P$ NMR and $^1H$ NMR spectra, which display respectively a single peak at 35.3 ppm and four distinct AB patterns for the bridging methylene groups (see SI). The $C_5H_5$ ring protons of **2** appear at relatively high field ($\delta$ = 2.76 ppm) in the $^1H$ NMR spectrum as a result of aromatic ring-current effects of the capsule. In contrast, the spectrum of the related bis-phosphine complex **4** (Figure 1) shows a much lower-field Cp signal ($\delta$ = 4.48 ppm).

The ultimate proof of the strong metal confinement in **2** came from a single-crystal X-ray diffraction study (Figure 2). In

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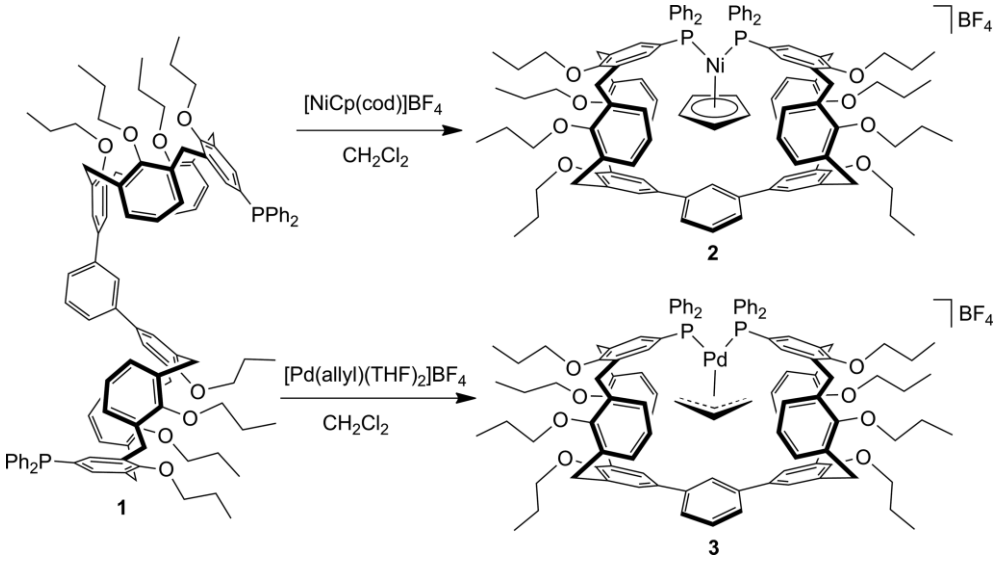



Scheme 1. Formation of capsular complexes with embedded metal centres.

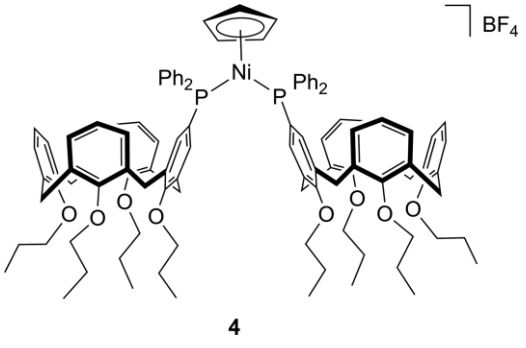



Figure 1. Formula of complex **4** containing two upper-rim phosphinated calix[4]arenes (**5**).

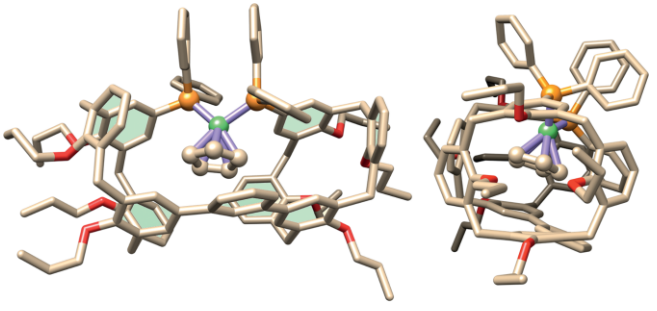


Figure 2. Molecular structure of the cationic complex **2** showing the encapsulated Ni($\eta^5$-$C_5H_5$) moiety; left: view perpendicular to the $NiP_2$ plane; right: view along the axis of one of the calixarene ends. Only one of the two isomers (A) present in the unit cell is shown. The uncoordinated $[BF_4]^-$ anion has been omitted for clarity.

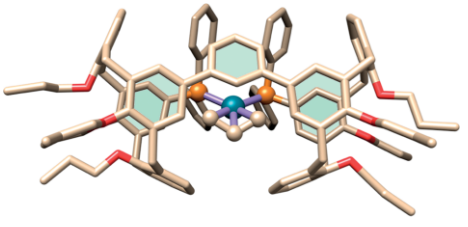
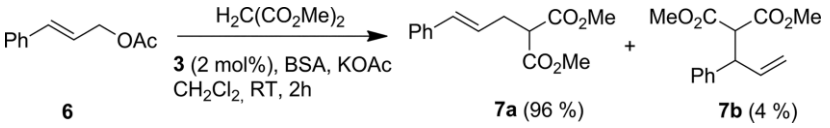


Figure 3. Molecular structure of the cationic palladium complex 3 ($[BF_4]^-$ anion not shown).

the unit cell, two inequivalent but only slightly different molecules (A and B) are present, both having their cyclopentadienyl unit embedded in the capsule formed by complexation. Each molecule has its Ni–($\eta^5$-$C_5H_5$) axis distinctly inclined towards one of the calixarene units, this enabling weak $\pi$–$\pi$ interactions to occur between the $C_5H_5$ ring and two (distal) phenol rings of the calixarene unit (shortest inter-ring C···C separations: 3.28 Å and 3.17 Å in isomer A; 3.3 Å and 3.5 Å in isomer B) as well as with the central phenylene ring. As the two calixarene units are equivalent on the NMR time scale, the Ni–$C_5H_5$ axis of **2** must alternate in orientation towards the two calixarene moieties. However, this motion could not be frozen out (variable temperature study carried out in $CD_2Cl_2$ in the range –60 °C – 25 °C, see SI).[14] The ligand bite angle of **2** (105.0° in A; 104.4° in B) is just a little larger than that observed for the PMP angle in $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (102.9°; see DOSNAB[15] in CCDC).[16] For comparison we also determined the solid-state structure of the related capsular complex [Pd($\eta^3$-$C_3H_5$)(**1**)]$BF_4$ (**3**) (Figure 3), which was formed quantitatively by reacting **1** with [Pd($\eta^3$-$C_3H_5$)$(THF)_2$]$BF_4$.[17] While for **3** the ligand bite angle value (104.6°) is very close to that of **2**, the organometallic part of the complex, i.e. the Pd–allyl moiety, is nearly symmetrically located within the capsule.

Significantly, the allyl group displays a specific orientation within its host, its central carbon atom pointing towards the most open part of the capsule's entry, thereby obviously minimising its steric interactions with the phenylene linker. The C···C separations between the terminal allylic carbon atoms and the closest carbon atoms of the phenylene moiety are 3.41 and 3.38 Å, respectively. Overall, the reactions leading to **2** and **3** constitute an illustration of the remarkable structuring properties of diphosphine **1**, which enables creation of a capsule upon chelation of a metal centre and, in the case of **3**, controlled orientation of the metal-bound allylic ligand.




Scheme 2. Palladium-catalysed alkylation of 3-phenylallyl acetate.

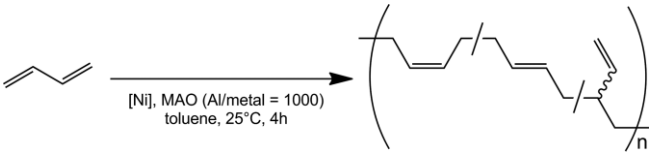
A question arises concerning the ability to achieve a catalytic reaction at such highly confined metal centres. Thus, we first assessed the palladium complex **3** in the alkylation of 3-phenylallyl acetate **6** with dimethyl malonate, a reaction for which two products were expected, **7a** and **7b** (Scheme 2). In $CH_2Cl_2$ at room temperature, metallocapsule **3** showed activities similar to those obtained with classical Pd/phosphine systems. Furthermore, the "linear" alkylation compound **7a** (which in its coordinated form fits better inside the cavity than the corresponding branched isomer) was formed with 96 % selectivity, a value which corresponds to a slightly higher proportion than that obtained with $[Pd(\eta^3\text{-}C_3H_5)(Ph_2PCH_2\ CH_2PPh_2)](BF_4)$ (91 %) under similar conditions. These findings suggest that the substrate used has good access to the embedded metal centre, although we have no formal proof that during catalysis the capsular shape is retained (vide infra).

We then turned our attention to metallocapsule **2**, which was found suitable for polymerisation reactions. Thus, once activated with methylaluminoxane (MAO/Ni = 1000:1) complex **2** becomes an efficient butadiene polymerisation catalyst, leading to a mixture of *cis*-1,4-, *trans*-1,4-, and 1,2-polybutadiene showing a classical distribution (89.4:6.5:4.1) (Table 1). Remarkably, when carrying out the polymerisation at room temperature, and by applying a butadiene pressure of 1 atm (4 μmol Ni, 20 mL of toluene), the catalytic system displayed an activity which was ca. 30–40 (!) times higher than that of the non-confined complexes $[Ni(\eta^5\text{-}C_5H_5)(dppe)](BF_4)$ and $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)_2](BF_4)$ (with the latter two complexes leading to comparable selectivities, see Table 1). The reason for the high activity of **2** compared with that of its bis-$PPh_3$ analogue is a matter of speculation. It is tempting to consider that the activity of **2** is related to its container structure. This notion is reinforced by the observation that the calixarene-based complex **4**, which contains two monodentate P(III)-ligands, provides, like the simple complex of $PPh_3$, a lower degree of activity[18] with respect to that of **2** (with unchanged selectivity, see Table 1). Of course, to retain a capsular structure during catalysis, both P atoms need to remain bonded to the nickel atom. Interestingly, on the basis of a theoretical study published in 1998,[19] the mechanism of butadiene polymerisation with $[Ni(\eta^3\text{-allyl})(PH_3)_2]^+$ (see SI) has been proposed to pass through $\eta^3$-allylic nickel intermediates containing a *single* phosphine ligand, the other phosphine having undergone dissociation. These theoretical findings are thus in contradiction with our deduction that both P atoms of **2** remain coordinated during catalysis. What we now propose is that the particular steric crowding imposed by a capsular structure favours the formation of $\eta^1$-allylic intermediates that precede the insertion step {notably complexes of the type $[Ni(\eta^1\text{-}CH_2\text{-}CH{=}CH\text{-}\boldsymbol{P})$ (chelating-**1**)(butadiene)]$BF_4$, in which ·***P*** represents a polymeric fragment}. This then enhances the rate of butadiene insertion. It is noteworthy that the ability of chelated metal units to form easily $\eta^1$-allyl complexes was recently demonstrated by Braunstein et al. [20] It should further be mentioned that the capsule which embeds the metal centre may itself behave as a butadiene receptor, thereby leading to an increased local substrate concentration of butadiene, which necessarily would impact on the reaction rate.

## Conclusions

We have shown that diphosphine **1** readily forms metallo-capsules when opposed to metal ions with two free, *cis*-configured binding sites. The superior activity of its capsular Ni(II)-π-allyl complex **2** as a catalyst for butadiene polymerisation compared to non-capsular but otherwise similar complexes implies that the capsular form and thus the binding of both phosphine centres in maintained during catalysis. It is particularly significant that encapsulation of the catalytic centre apparently does not result in any inhibition of access and we suggest that any steric restraints imposed by encapsulation may in fact accelerate reaction by favouring the involvement of $\eta^1$-allylic intermediates.

Table 1. Butadiene polymerisation using $[NiCp(phosphine)_2]^+$/MAO catalysts.[a]




| Entry | complex | Polymer Yield [g] | Activity [g/mol(Ni) h] | $M_n$ | $M_w/M_n$ (monomodal) | 1,4-*cis* [%] | 1,4-*trans* [%] | 1,2 [%] |
|---|---|---|---|---|---|---|---|---|
| 1 | $[Ni(\eta^5\text{-}C_5H_5)(\mathbf{1})]BF_4$ (**2**) | 2.841 | 178000 | 37300 | 2.21 | 89.4 | 6.5 | 4.1 |
| 2 | $[Ni(\eta^5\text{-}C_5H_5)(dppe)]BF_4$ | 0.075 | 4670 | 31800 | 1.63 | 89.1 | 6.5 | 4.4 |
| 3 | $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)_2]BF_4$ | 0.096 | 6010 | 33900 | 1.77 | 88.0 | 7.0 | 5.0 |
| 4 | $[Ni(\eta^5\text{-}C_5H_5)(\mathbf{5})_2]BF_4$ (**4**) | 0.199 | 12500 | 59200 | 1.66 | 88.5 | 6.3 | 5.2 |

[a] Conditions: [Ni] ($4 \times 10^{-3}$ mmol), MAO (4 mmol), butadiene (1 atm), toluene (20 mL), 25 °C, 4 h. Complex **4** is shown in Figure 1.

Theoretical investigations may be helpful to confirm these hypotheses.

## Experimental Section

**General Methods:** All reactions were performed under nitrogen in Schlenk tubes. 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 $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on FT Bruker AVANCE 300 and AVANCE 400 instruments. $^1H$ NMR spectroscopic data were referenced to residual protiated solvents [7.26 ppm for $CDCl_3$, 7.16 ppm for $C_6D_6$ and 5.32 for $CD_2Cl_2$], $^{13}C$ chemical shifts are reported relative to deuterated solvents [77.0 ppm for $CDCl_3$, 128.06 ppm for $C_6D_6$ and for 54.00 $CD_2Cl_2$] and the $^{31}P$ NMR data are given relative to external $H_3PO_4$. Mass spectra were recorded either on a Maldi TOF spectrometer (MALDI-TOF) using α-cyano-4-hydroxycinnamic acid as matrix, or on a Bruker MicroTOF spectrometer (ESI-TOF) using $CH_2Cl_2$, MeCN or MeOH as the solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UMR 7177 CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus. Ligand **1**,[17] palladium complex **3**,[17] [($\eta^5$-$C_5H_5$)Ni(cod)$BF_4$],[21] [Ni($\eta^5$-$C_5H_5$)(dppe)]$BF_4$,[22] [Ni($\eta^5$-$C_5H_5$)($PPh_3$)$_2$]-$BF_4$,[23] were prepared according to previously reported procedures. An optimised preparation of **1** is given as supplementary information. The catalytic solutions of the allylic alkylations were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm). GPC analyses were carried out with a Waters apparatus. Size Exclusion Chromatography (SEC) measurements were performed on a Shimadzu Prominence System equipped with 5 serial mixed B PLgel columns. Detection was performed by a differential refractometer (RID10A, Shimadzu), a UV/Vis PDA detector (SPD-20A, Shimadzu), a multi-angl-light scattering (MALS) detector (DAWN TREOS, Wyatt techn.) and a on-line viscosimeter (Viscostar-II, Wyatt Techn.). The flow rate was 1 mL/min and high purity THF was used as eluent. The columns were calibrated with 16 narrow polystyrene standards (Polymer Lab).

***cis-P,P′*-(η⁵-Cyclopentadienyl)-[1,3-bis(5-diphenylphosphino-25,26,27,28-tetrapropoxy-calix[4]aren-17-yl)benzene]nickel (II) Tetrafluoroborate (2)**: A solution of [($\eta^5$-$C_5H_5$)Ni(cod)]$BF_4$ (0.030 g, 0.092 mmol) in $CH_2Cl_2$ (100 mL) and a solution of 1,3-bis(5-diphenylphosphino-25,26,27,28-tetrapropoxy-calix[4]aren-17-yl)benzene (0.150 g, 0.092 mmol) in $CH_2Cl_2$ (100 mL) were simultaneously added under vigorous stirring over a period of 2 h to a 1000 mL Schlenk flask containing 500 mL of $CH_2Cl_2$. The reaction mixture was stirred at room temperature for 16 h. The solvent was evaporated to dryness and the resulting olive green solid was washed with $Et_2O$, then dried under vacuum (0.152 g, 90 %). $^1H$ NMR (600 MHz, 253K, $CDCl_3$) (owing to a dynamic molecule, all $^1H$ NMR signals are somewhat broad at 253K; see also SI): 7.41–6.58 (m, 42H, $PPh_2$, H of phenylene, *para* H of $OAr_{calix}$, *meta* H of $OAr_{calix}$), 6.10 (broad s, 2H, *para* H of $OAr_{calix}$), 4.53 and 3.28 [AB spin system, 4H, Ar$CH_2$Ar, $^2J$(AB) = 12 Hz], 4.55 and 3.34 [AB spin system, 8H, Ar$CH_2$Ar, $^2J$(AB) = 10.8 Hz], 4.36 and 2.96 [AB spin system, 4H, Ar$CH_2$Ar, $^2J$(AB) = 12 Hz], 4.25, 4.06, 3.64 and 3.62 (4m, 16H, $OCH_2$), 2.67 (s, 5H, Cp), 2.17, 2.07 and 1.88 (3m, 16H, $CH_2CH_2CH_3$), 1.04 and 0.90 (2m, 24H, $CH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta$ = 35.21 (s, $PPh_2$). $^{13}C\{^1H\}$ NMR (150.90 MHz, $CDCl_3$) $\delta$ = 157.64, 157.03, 156.92 and 155.56 (4s, $C_q$-$OCH_2$), 137.96- 120.67 ($PPh_2$ and arom. C's), 96.78 (s, Cp), 78.15, 78.11, 76.93 and 76,25 (4s, $OCH_2$), 32.07, 31.27, 30.80 and 30.67 (4s, Ar$CH_2$Ar), 23.58, 23.54, 23.23 and 22.869 (4s, $CH_2CH_3$), 10.79, 10.72, 10.03 and 9.89 (4s, $CH_3$). MS (ESI-TOF): *m/z* (%) 1750.79 (100) [M – $BF_4$]$^+$, expected isotopic profile. Elemental analysis: Found: C, 75.32; H, 6.84. Calc. for $C_{115}H_{121}BF_4NiO_8P_2$ ($M_r$ = 1838.63) C, 75.12; H, 6.63 %. Single crystals of the product were grown as plates by slow diffusion of pentane into a dichloromethane solution of the complex at room temperature.

***P,P*-(η⁵-Cyclopentadienyl)-bis-{5-(diphenylphosphino)-25,26,27,28-tetra-propoxycalix[4]arene}nickel (II) Tetrafluoroborate (4)**: A solution of 5-diphenylphosphino-25,26,27,28-tetrapropoxy-calix[4]arene (**5**) (0.152 g, 0.195 mmol) in $CH_2Cl_2$ (10 mL) was added to a solution of [($\eta^5$-$C_5H_5$)Ni(cod)]$BF_4$ (0.032 g, 0.098 mmol) in $CH_2Cl_2$ (10 mL). After stirring for 1 h, the solution was concentrated to ca. 2 mL and hexane (10 mL) was added. An olive green precipitate formed, which was separated by filtration through silica, then dried under vacuum (0.167 g, yield 97 %). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.38–6.39 (36 H, $PPh_2$ and *p*- and *m*-H of $OAr_{calix}$), 6.39 (m, 4H, *m*-H of $OAr_{calix}$ in distal position to phosphinated Ar), 5.98 (t, 2H, *p*-H of $OAr_{calix}$ in distal position to phosphinated Ar, $^3J_{H\text{-}H}$ = 8Hz), 4.47 (s, 5H, Cp), 4.44 and 3.16 [AB spin system, 8H, Ar$CH_2$Ar, $^2J$(AB) = 12 Hz], 4.43 and 3.07 [AB spin system, 8H, Ar$CH_2$Ar, $^2J$(AB) = 12 Hz], 3.94 and 3.73 (2m, 2x8 H, $OCH_2$), 1.94 (2 m, 2 × 8 H, $OCH_2CH_2CH_3$), 1.07 (t, 6H, $CH_3$), 1.03 (t, 6H, $CH_3$), 0.95 (t, 12H, $CH_3$, $^3J$ = 8 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$) $\delta$ = 34.4 (s, $PPh_2$). $^{13}C$ NMR (125.77 MHz, $CDCl_3$) $\delta$ = 158.58, 156.90 and 155.85 (3s, Cq-$OCH_2$), 136.48–120.08 ($PPh_2$ and arom. C's), 97.66 (s, Cp), 77.71 and 76.78 (2s, $OCH_2$), 31.04 and 30.95 (2s, Ar$CH_2$Ar), 23.55, 23.48 and 23.14 (3s, $CH_2CH_3$), 10.70, 10.66 and 10.16 (3s, $CH_3$). MS (HR-MS): *m/z* (%) 1676.7745 (100) [M – $BF_4$]$^+$, expected isotopic profile. Elemental analysis: calcd. for $C_{109}H_{119}O_8P_2NiBF_4$ C 74.19, H 6.79 Found: C 73.87, H 6.94.

### Single-Crystal X-ray Diffraction

**Crystal Data for 2:** Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a $CH_2Cl_2$ solution of the complex: $C_{230}H_{242}B_2F_8Ni_2O_{16}P_4$·1.5$C_5H_{12}$, 2*M* = 3785.36, orthorhombic, space group $P_{bca}$, *a* = 30.5294(7), *b* = 38.6460(10), *c* = 38.646(10) Å, $\alpha = \beta = \gamma$ = 90.00°, *V* = 44909(2) Å$^3$, *Z* = 8, $\mu$ = 0.260 mm$^{-1}$, *F*(000) = 16088. Crystals of the compound were mounted on an Oxford Diffraction CCD Sapphire 3 Xcalibur diffractometer. Data collection with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) was carried out at 100 K. 131039 reflections were collected (2.50 < $\theta$ < 23.0°), 28205 being found to be unique (merging *R* = 0.123). The structure was solved with SHELXL-2016.[24] Final results: $R_1$ = 0.098, $wR_2$ = 0.312, goodness of fit = 0.965, 2426 parameters, residual electron density: min./max. = –0.533/1.752 e Å$^{-3}$. The level A alerts in the checkcif arise from disordered atoms in both the four *O*-alkyl substituents and the solvent molecules. The main difficulty with this compound was the very marked decrease of the intensities observed even at 100K with increasing theta values.

**Crystal Data for 3:** Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a $CH_2Cl_2$ solution of the complex: $C_{452}H_{484}B_4F_{16}O_{32}P_8Pd_4$·$CH_2Cl_2$·3$C_5H_{12}$, *M* = 7750.32, monoclinic, space group *Pn*, *a* = 16.9631(3), *b* = 35.9731(7), *c* = 37.8148(7) Å, $\beta$ = 91.03°, *V* = 23071.4(7) Å$^3$, *Z* = 2, $\mu$ = 0.257 mm$^{-1}$, *F*(000) = 8176. Crystals of the compound were mounted on an Oxford Diffraction CCD Sapphire 3 Xcalibur diffractometer. Data collection with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) was carried out at 110 K. 201478 reflections were collected (2.6 < $\theta$ < 27.0°), 92585 being found to be unique (merging *R* = 0.105). The structure was solved with SHELXL-2016/4.[24] The elemental cell contains four distinct, but almost identical molecules. The main difficulty in solving this structure came from the large thermal motion of some *O*-propyl groups and the [$BF_4$]$^-$ anions. It was necessary to fix some atoms

and to apply restraints in order to avoid instability during refinements. The level A alerts in the checkcif are thus mainly due to the thermal motion of the *O*-propyl groups and the $[BF_4]^-$ anions, but also to the disordered $CH_2Cl_2$ molecule. Note that this data collection was made at 110K. Another data collection was made at 100K: at this temperature, we observed a phase transition [beta angle decrease from 91.034(2) to 90.277(1)]. The corresponding space group was again unambiguously *Pn*, but seemingly the transition went to orthorhombic *Pnn*2. Final results: $R_1$ = 0.067, $wR_2$ = 0.191, goodness of fit = 0.602, 4518 parameters, residual electron density: min./max. = –0.821/1.140 e Å$^{-3}$.

CCDC 771989 (for **2**), and 768418 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Allylic Alkylation Experiments:** A $CH_2Cl_2$ solution (15 mL) of $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{1})]BF_4$ (0.019 g, 0.01 mmol), cinnamyl acetate (0.176 g, 1.00 mmol), dimethylmalonate (0.396 g, 3.00 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (0.610 g, 3.00 mmol) and a catalytic amount of KOAc was stirred at room temperature for 2 h. The solution was then diluted with a saturated aqueous solution of $NH_4Cl$ (10 mL) and $CH_2Cl_2$ (10 mL). To determine the conversion and the product distribution by GC, decane (0.10 mL) was added to the organic phase. GC analysis gave the following product distribution: dimethyl [(2E)-3-phenylprop-2-en-1-yl]propanedioate: 96 %; dimethyl (1-phenylprop-2-en-1-yl)malonate: 4 %.

**Butadiene Polymerisation:** To a 25-mL Schlenk flask containing a nickel complex (4 μmol) was added toluene (18 mL). After the mixture was frozen with liquid nitrogen, the inner gas was evacuated and the Schlenk flask was backfilled with butadiene by using a balloon filled with butadiene gas. The mixture was warmed to room temperature, and a solution of MAO (Al/Ni = 1000) in toluene solution (2 mL) was added to the mixture. After stirring the mixture at room temperature (400 rpm) for 4 hours, the reaction was quenched by adding MeOH (50 μL). The solution was then poured into a HCl/MeOH solution (HCl/MeOH = 1:4 v/v, 150 mL). The resulting precipitate was collected by filtration and dried in vacuo overnight. The polymer distribution was determined using $^{13}C\{^1H\}$ NMR.[25] The molecular weights (*M*n) and molecular weight distributions (*M*w/*M*n) of the polymer were measured by gel permeation chromatography (GPC). The *M*n and *M*w/*M*n values were determined using the polystyrene calibration.

## Acknowledgments

We gratefully acknowledge financial support from the University of Strasbourg Institute for Advanced Study (to D. M.) and from the Frontier Research in Chemistry Foundation, Strasbourg (postdoctoral grant to F. E.).

**Keywords:** Nickel · Supramolecular chemistry · Molecular containers · Calixarenes · Butadiene polymerisation · Allylic alkylation

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Received: October 4, 2019

**Molecular Containers**

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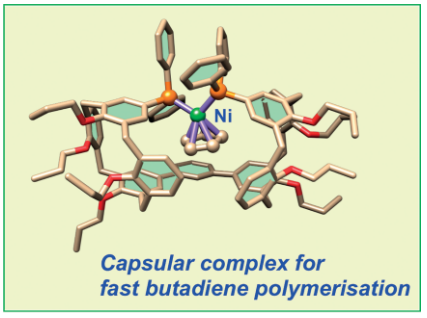
**Metallated Container Molecules: A Capsular Nickel Catalyst for Enhanced Butadiene Polymerisation**




**A *covalently constructed* capsular nickel catalyst** was obtained in one step from a double-calixarene-derived diphosphine. Its activity in butadiene polymerisation was found to be 40 times higher than that of related nickel complexes devoid of a capsular structure.

**DOI: 10.1002/ejic.201901074**