DALTON
FULL PAPER

Positioning of transition metal centres at the upper rim of cone-shaped calix[4]arenes. Filling the basket with an organometallic ruthenium unit

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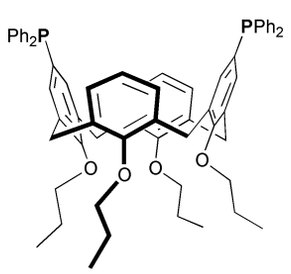
A series of calix[4]arenes bearing diphenylphosphino groups tethered at the upper rim have been prepared by treatment of 5,11,17,23-tetrabromo-25,26,27,28-tetrapropoxycalix[4]arene with Bu^{t}Li (or Bu^{n}Li) followed by reaction with PPh_2Cl. The tetraphosphinated derivative **3** was found suitable for the formation of tetranuclear species, notably [**3**·$(AuCl)_4$], [**3**·$\{RuCl_2(p\text{-cymene})\}_4$], and [**3**·$\{PdCl(o\text{-}C_6H_4CH_2NMe_2)\}_4$], all possessing an apparent C_{4v}-symmetry in solution. Reaction of $[RuCl_2(p\text{-cymene})]_2$ with the diphosphines 5,17-di-X-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (X = H, **1**; X = Br, **4**) afforded the C_{2v}-symmetrical dinuclear complexes [**1**·$\{RuCl_2(p\text{-cymene})\}_2$] and [**4**·$\{RuCl_2(p\text{-cymene})\}_2$], respectively. Reaction of the non-brominated diphosphine **1** with $[PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$ gave the complex [**1**·$\{PdCl(o\text{-}C_6H_4CH_2NMe_2)\}_2$]. Reaction at high dilution of $[PtCl_2$(1,5-cyclooctadiene)] with **4** or **1** resulted in quantitative formation of the corresponding *cis*-chelate complexes [**4**·$PtCl_2$] (**12**) and [**1**·$PtCl_2$] (**13**), respectively. The *trans* version of **13** could also be obtained, provided that $[PtCl_2(PhCN)_2]$ was used as starting complex. In the solid state, the $PtCl_2$ unit of **12** is directed towards one bromine atom, resulting in a highly unsymmetrical calixarene structure where the metal plane is nearly parallel to the calix reference plane. The NMR spectra of **12** and **13** show an apparent C_{2v}-symmetrical structure, suggesting a fast fan-like motion in solution of the metal plane about the P ··· P axis. Similar dynamics are likely to occur in the related cationic complexes [**1**·Rh(norbornadiene)]BF_4 (**15**) and [**1**·Pd(Me-allyl)]BF_4 (**16**). As shown by variable temperature studies carried out on **12** and **16**, these dynamics couple with a concomitant, restricted rotation of the two PPh_2 units about their coordination axis. The latter motion is probably a result of steric interactions within the phosphorus environment, two PPh rings being in competition for occupation of the cavity entrance. Reaction of the expanded cavity 5,11,17-tribromo-23-diphenylphosphino-25,26,27,28-tetrapropoxycalix[4]arene **5** with $[RuCl_2(p\text{-cymene})]_2$ afforded the monophosphine complex [**5**·$RuCl_2(p$-cymene)]. In solution as well in the solid state, the *p*-cymene ligand fills the calixarene basket.

Calixarene-derived phosphine ligands have led to an extremely rich coordination chemistry.[1–4] One current development rests on the anticipation that the covalent linking of such a receptor to a transition metal centre could lead to supramolecular catalysts of industrial relevance.[4,5] As a first step to this goal we have recently synthesized a series of complexes in which a metal unit is fixed in a rigid manner near the upper rim of a calix-[4]arene kept in the so-called cone conformation. This has led to several metallo-cavitands where the metal first coordination sphere is partly sequestered inside the calixarene core.[6] Structures of this type were first reported for the 5,17-diphosphinated calix[4]arene **1**, a ligand which readily forms chelate complexes having *trans*-arranged phosphorus atoms. Thus for example, we found that diphosphine **1** reacts with $[RuCl_2(CO)_2]_n$ resulting in a calixarene that contains an entrapped Ru–C≡O fragment. An X-ray study showed that the carbonyl nested inside the cavity is sandwiched between two facing phenol units separated by only 5.5 Å. Note, other calix-arene complexes containing non-phosphorus complexing units were recently used for the partial or total encapsulation of metal-bonded substrates.[7–9] This topic has also been extended to metallo-cyclodextrins.[10]



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In the present study we report on the synthesis and coordinative properties of calixarenes containing one, two or four phosphino groups tethered at the upper rim of a calix[4]arene. The directed positioning of transition metal fragments at the

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cavity entrance is described for some of these ligands, including a monophosphine derivative which was shown to be suitable for hosting a (*p*-cymene)–ruthenium moiety. Furthermore, this work demonstrates, for the first time, that diphosphine **1** as well as a related ligand allow *cis*-chelation across the cavity, resulting in the formation of highly unsymmetrical calix[4]arenes. It should be mentioned that related upper-rim phosphinated calixarenes have been reported recently,[5,11,12] but with none of them was entrapment of metal–organic fragments inside the cavity achieved. All calixarenes reported herein adopt a cone conformation. Conformational assignments were made using well-established rules based on ^{1}H and ^{13}C NMR data.[6,13,14]

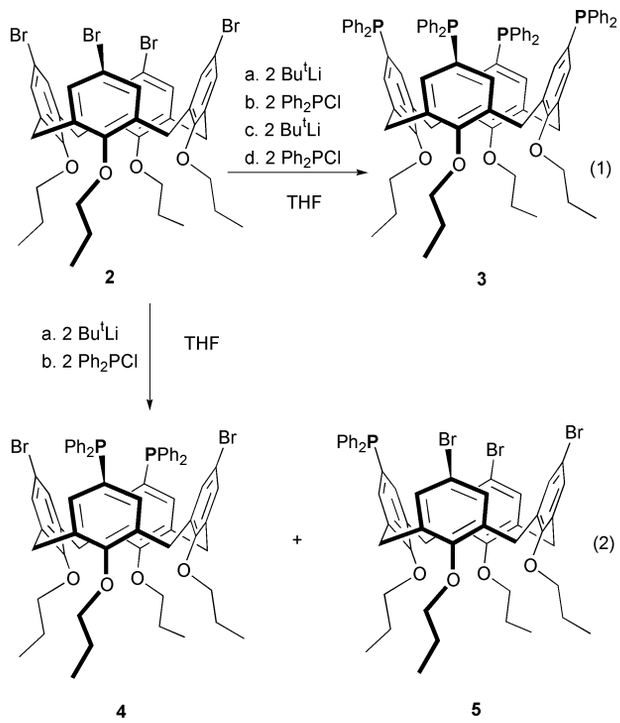
Results and discussion

Introducing P(III) centres on the upper rim of calix[4]arenes

We recently reported a straightforward preparation of tetraphosphine **3** which is based on the following two steps: (i) introduction of four phosphoryl units by reaction of **2** with $Ph_2POEt/NiBr_2$ in refluxing benzonitrile; (ii) reduction of the thus formed phosphine oxide with $PhSiH_3$.[15,16] The phosphorylation step was inspired by a method originally developed by Tavs.[17] We have now found that **3** may also be prepared in a convenient *one-pot* synthesis by stepwise addition to **2** of two equiv. of Bu^{t}Li and two equiv. of Ph_2PCl, then by repeating this sequence after 10 h reaction time [eqn. (1)]. This one-pot procedure afforded **3** in 78% yield (after workup). Attempts to achieve a direct tetraphosphination using four equiv. of the reagents (Bu^{t}Li, PPh_2Cl) were not satisfactory, since these afforded a mixture of compounds in which only small amounts of **3** were present. Similar observations were recently made by Harvey *et al.*[18] It is likely that tetralithiation cannot take place due to steric congestion about the partially lithiated *cone* intermediate(s) formed once the first amounts of Bu^{t}Li have been added. This situation contrasts with the results of Hamada[19] and Tsuji[20] who found that tetraphosphination using Bu^{n}Li/PPh_2Cl can be achieved in one step when starting from conformationally *non-rigid* analogues of **2**. However, in this case the end-product is a mixture of equilibrating conformers. The molecular structure of tetraphosphine **3** was reported in our preliminary work.[15] Consistent with our findings, the diphosphinated compound **4** could be prepared in good yields by reacting **2** with two equiv. of Bu^{t}Li and two equiv. of PPh_2Cl [eqn. (2)]. The NMR data of this compound are in full agreement with a C_{2v}-symmetrical molecule. The workup of the reaction required two recrystallisations in order to eliminate small quantities of a side product, namely monophosphine **5**, formed in less than 5% yield. The synthesis of the latter could be improved up to 10% by performing the Br/Li exchange with Bu^{n}Li (one equiv.) instead of Bu^{t}Li. In this case no diphosphinated product was formed. In keeping with the presence of a mirror plane, the ^{1}H NMR spectrum of monophosphine **5** displays three patterns for the *m*-aryl-*H* of the calixarene moiety and two AB systems for the $ArCH_2$ protons. Other valuable NMR data can be inferred from the Experimental section.

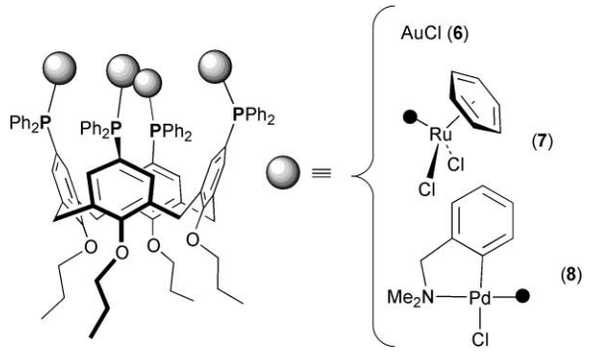
Complexation studies

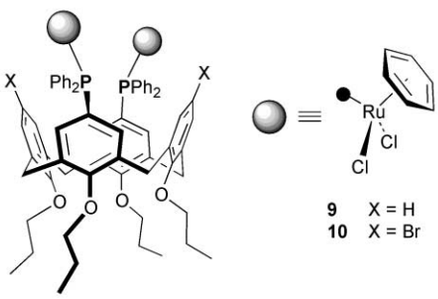
Ligand **3** defines a complexation domain which, *a priori*, appears suitable for maintaining four discrete metal centres in close proximity, and indeed tetranuclear complexes could be synthesized from this tetraphosphine. Thus the three complexes **6**, **7** and **8** were readily obtained by reacting **3** with [AuCl(THT)] (THT = tetrahydrothiophene), $[RuCl_2(p\text{-cymene})]_2$ and $[PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$, respectively. They were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis (see the Experimental section). As deduced from the NMR spectra the calixarene units keep the apparent C_{4v} symmetry found in the free ligand, which actually corresponds to a fast $C_{2v} \rightleftharpoons C_{2v}$ equilibrium.[2] The NMR spectra of complex **8** revealed that the four $PdCl(o\text{-}C_6H_4CH_2NMe_2)$ moieties are equivalent, suggesting that despite the relative bulkiness of these fragments there is no rotational barrier about the P–Pd bond. This situation contrasts with that encountered in a related calix[4]arene complex in which four "$PdCl(o\text{-}C_6H_4CH_2NMe_2)$" moieties, connected to the *lower* rim *via* $-CH_2PPh_2$ ligands, do not move freely.[21]

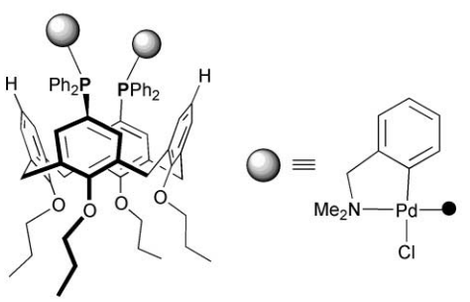


Attempts to perform, with **3**, the synthesis of complexes having a nuclearity smaller than four, for instance by addition of sub-stoichiometric amounts of ligand to a starting complex, only led to mixtures of products that could not be separated. On the other hand, diphosphines **1** and **4** could be used for the selective synthesis either of dinuclear or mononuclear complexes. For example, the dinuclear ruthenium complexes **9** and **10** were obtained in high yield from $[RuCl_2(p\text{-cymene})]_2$, while complex **11** was quantitatively formed by reacting **1** with $[PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$. The NMR data of **9**–**11** are fully consistent with C_{2v}-symmetrical structures. The suitability of **4** to form mononuclear complexes was first assessed towards Pt(II). Thus reaction of a 10^{-5} M dichloromethane solution of $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene) or $[PtCl_2(PhCN)_2]$, with one equiv. of **4** afforded complex **12** in high yield [eqn. (3)]. When the reaction was not carried out at high dilution, oligomeric material was formed, eqn. (4) (see Experimental).

Typically for a monomer, the NMR spectra of complex **12** display sharp signals. The observed *J*(PPt) coupling constant of 3621 Hz is in agreement with *cis*-arranged phosphorus atoms. This stereochemistry was confirmed by an X-ray diffraction study. The *cis* configuration (PMP angle *ca.* 100°) results in a highly unsymmetrical calixarene structure (Fig. 1), with the $PtCl_2$ unit approaching one of the two brominated walls and the coordination plane being nearly parallel to the calix reference plane. The calixarene core of **12** is remarkably distorted, the interplane angle between the ArBr planes being *ca.* 115°; in comparison, the phenol rings bearing the phosphines are slightly bent toward the interior of the cavity (dihedral angle: 22°). In order to minimize steric interaction with the calixarene framework, the two phosphino groups do not occupy equivalent positions in the structure. Thus a single phenyl ring fills the cavity entrance, making the whole structure C_1-symmetric in the solid state. Surprisingly, the ^{1}H and ^{13}C NMR spectra of **12** reveal an apparent C_{2v}-symmetry, which of course is not







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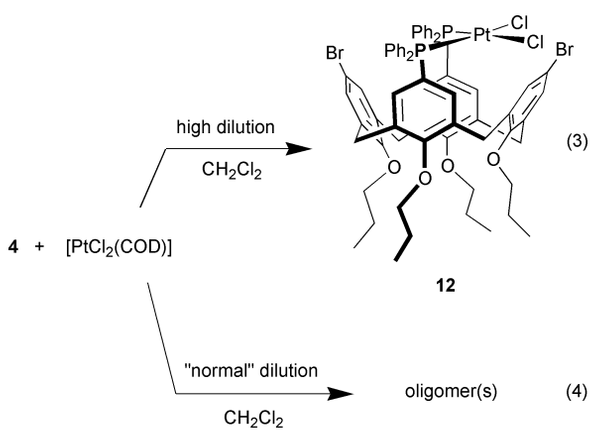


consistent with the solid state structure shown in Fig. 1. These observations suggest that a rapid fan-like motion of the metal plane about the PP axis takes place in solution, resulting in an averaged C_{2v} structure (Scheme 1). Interestingly, while the room temperature ^{31}P NMR (202 MHz) spectrum of **12** displays an A_2X pattern [X = Pt, $J(P^{195}Pt)$ = 3621 Hz], its signals broaden on lowering the temperature, coalesce at −40 °C, and finally split into a sharp ABX pattern [$J(PP')$ = 16 Hz, $J(P^{195}Pt) \approx 3530$ Hz, $J(P'^{195}Pt) \approx 3730$ Hz]. The same reduction of symmetry was also observed by ^{1}H NMR and is consistent with the C_1 symmetry found in the solid state. A plausible explanation for these findings is that the two PPh_2 units undergo a restricted (reversible) rotation about their coordination axis as shown in Scheme 2. This motion is likely to minimize steric interactions

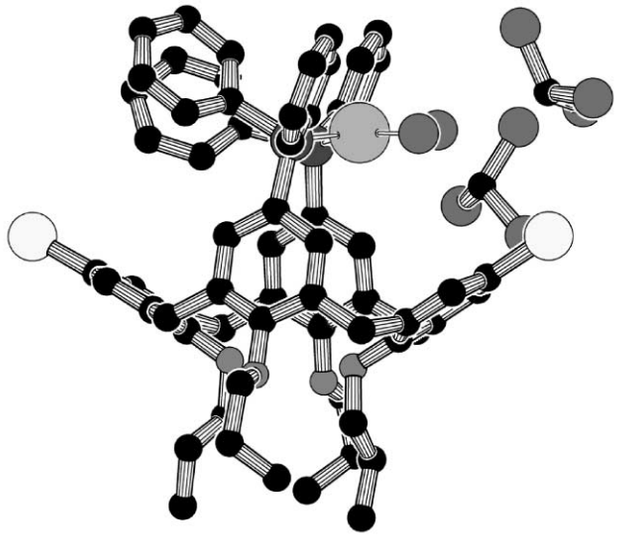
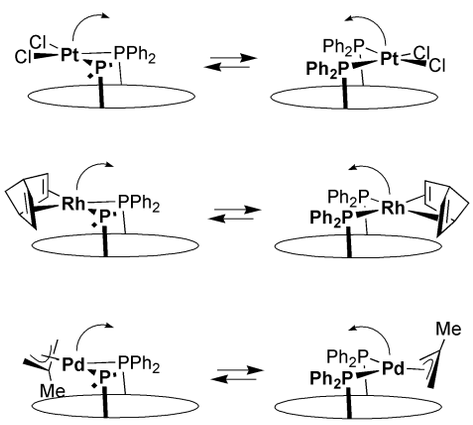
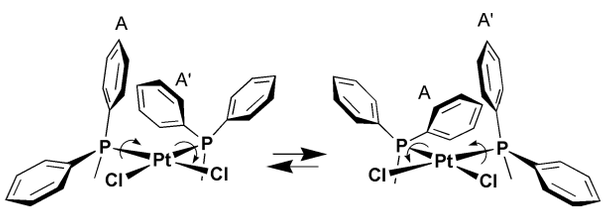


Fig. 1 Molecular structure of [$PtCl_2$·**4**] (**12**). The view also shows the two $CHCl_3$ solvates that lie close to the $PtCl_2$ unit.



Scheme 1 Proposed motion of the coordination plane in complexes **12**, **15** and **16**.

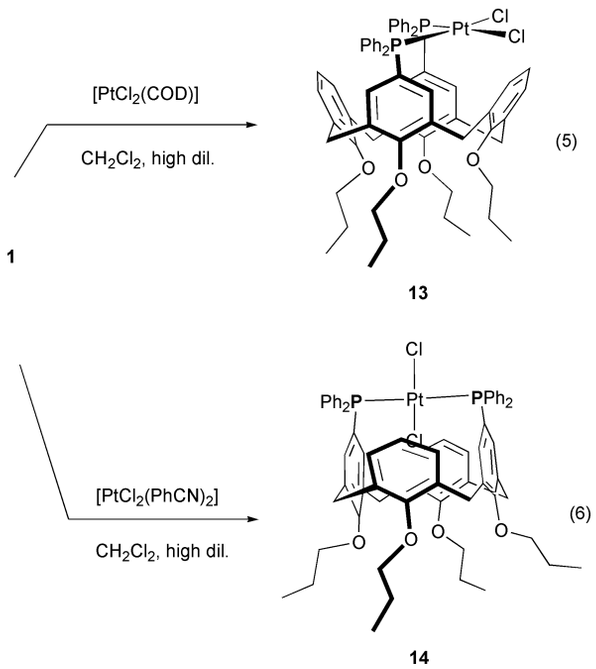


Scheme 2 Restricted rotation of the PPh_2 groups about the P–Pt bonds.

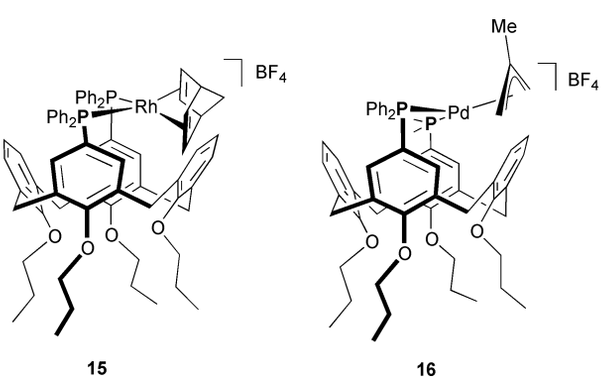
within the phosphorus environment, resulting in two PPh rings (A and A′) that compete for occupation of the cavity entrance. The energy barrier[22] for this phenomenon is $\Delta G^{\neq}$ = 9.9 kcal mol^{-1}.

It is noteworthy that the *trans* version of complex **12** could not be prepared, neither *via* a direct synthesis, nor by isomerization. Interestingly, with the related non-brominated ligand **1**, both stereochemistries, *cis* and *trans*, could be obtained. The selective formation of **13** or **14** [eqns. (5) and (6)] was shown to depend on the starting complex, [$PtCl_2$(COD)] yielding **13** and [$PtCl_2(PhCN)_2$] affording **14**. Again these preparations had to be carried out at high dilution. The reason why diphosphine **4** selectively results in a *cis* instead of a *trans* isomer remains unclear. It is likely that after coordination of a first P(III) atom the *bulky* bromine atoms of **4** are pushed away from the metal centre, hence generating a highly flattened calixarene. This in turn produces a structure with a short P ··· P separation inappropriate for *trans* chelation. It is likely that bromine repulsion from the centre of the cavity is amplified by solvation

effects. Note, in the solid state, **4** crystallizes with two $CHCl_3$ molecules that lie close to the $PtCl_2$ unit, each chloride ligand being associated to a single chloroform solvate (calculated $Cl_3CH \cdots ClPt$ separations: 2.78 Å and 2.69 Å, respectively).



To extend our knowledge on the coordinative properties of 5,17-diphosphinated calixarenes, we also studied the reaction of diphosphine **1** with the cationic complexes $[Rh(nbd)(thf)_2]BF_4$ and $[Pd(\eta^3\text{-Me-allyl})(thf)_2]BF_4$. These complexes possess very labile ligands, and are therefore expected to favor chelation over oligomer formation when reacted with diphosphines.[23] Indeed these reactions afforded quantitatively complexes **15** and **16**, respectively. The two FAB mass spectra showed the peaks expected for the corresponding $[M - BF_4]^+$ ions. As already observed for **12**, the NMR data of **15** are in keeping with a C_{2v}-symmetrical compound, suggesting the occurrence of dynamics that displace the rhodium(nbd) unit from one side of the calixarene to the other (Scheme 1).



For complex **16**, the solid state structure of which is shown in Fig. 2, the interpretation of the NMR spectra is made more difficult owing to the presence of an allyl group. In this case the room temperature spectrum reveals an apparent C_s-symmetry which in fact is consistent both with a static structure as found in the solid state, as well as a fluxional structure in which the metal plane oscillates rapidly about the $P \cdots P$ axis, provided that there is no "allyl rotation". This latter point was confirmed by ROESY experiments. Hence we have no definitive answer to the question whether the metal plane moves as shown in Scheme 1, although this hypothesis seems very reasonable. It should be mentioned that the 2D ROESY spectrum does not

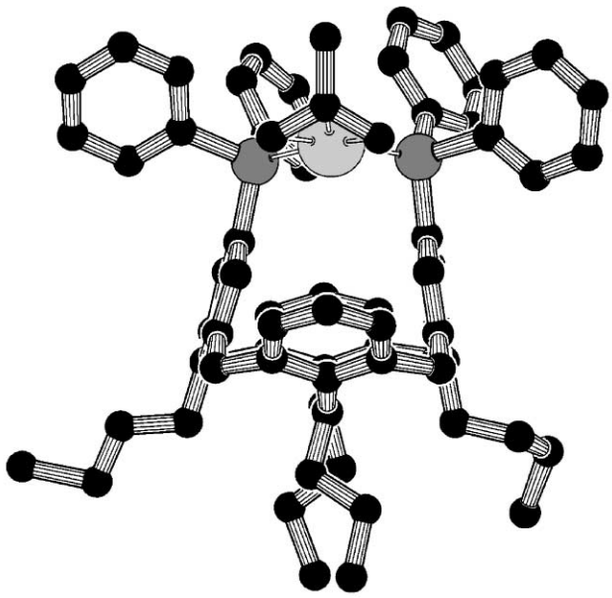


Fig. 2 Molecular structure of $[Pd(Me\text{-allyl})\cdot\mathbf{1}]BF_4$ (**16**) (BF_4 anion and $CHCl_3$ solvate not shown).

display significant correlations between the *Me*(allyl) group and the aromatic H atoms of the calixarene skeleton. Thus, should a motion as shown in Scheme 1 occur, then the two exchanging isomers would probably be unequally populated. Finally, we noted that on lowering the temperature both the ^{31}P and ^1H NMR spectra of **16** first broaden, then coalesce and eventually become sharp, the patterns being typically that of a C_1-symmetrical calixarene (Fig. 3). These results are consistent

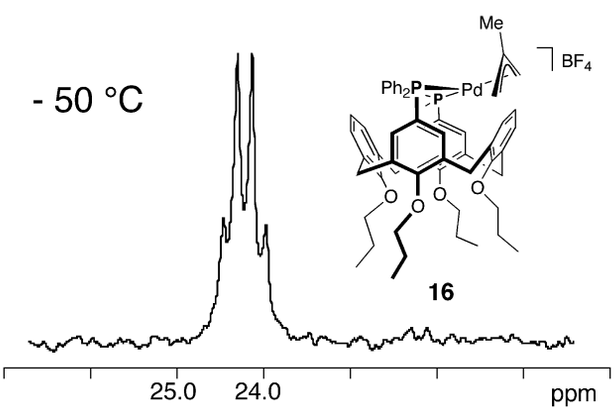
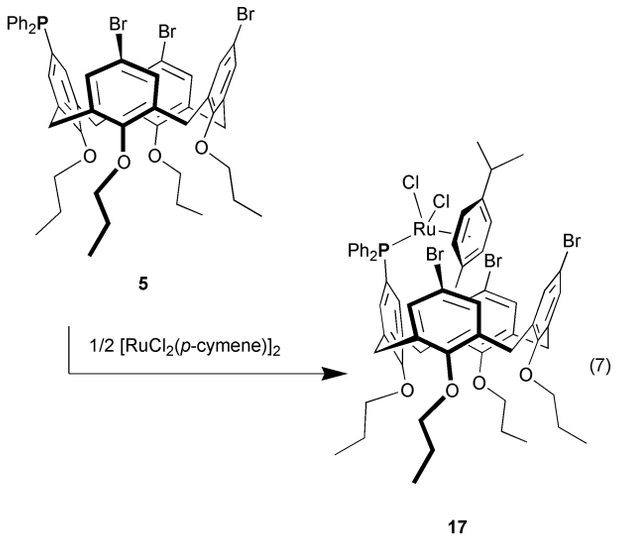


Fig. 3 Low temperature ^{31}P NMR spectrum (CD_2Cl_2, 202 MHz) of complex **16**.

with the PPh_2-dynamics already proposed for **12** in Scheme 2. The free enthalpy of activation is slightly higher than that found for **12** ($\Delta G^{\neq} = 11.2$ kcal mol^{-1}).

The complexation properties of monophosphine **5** were also evaluated. Bearing three bromine substituents located at the upper rim, this calixarene may be regarded as an expanded calix[4]arene cavity. Its ability to nest an organometallic unit was checked using $[RuCl_2(p\text{-cymene})]_2$. Reaction of this complex with **5** afforded **17** in 85% yield [eqn. (7)] which was characterized by a single crystal X-ray diffraction study.

As shown in Fig. 4, the Ru–P vector pointing towards the calixarene axis, and hence the "$RuCl_2$(*p*-cymene)" unit, sits within the four upper rim substituents (Br, Br, Br, P). Incidently, one end of the *p*-cymene ligand lies inside the deepened cavity. The partial encapsulation of the "$RuCl_2$(*p*-cymene)" moiety persists in solution, as deduced from the ^1H NMR spectrum which shows that the $MeC_6H_4Pr^i$ group as well as the neighbouring *ortho*-protons, both apically sited above two facing



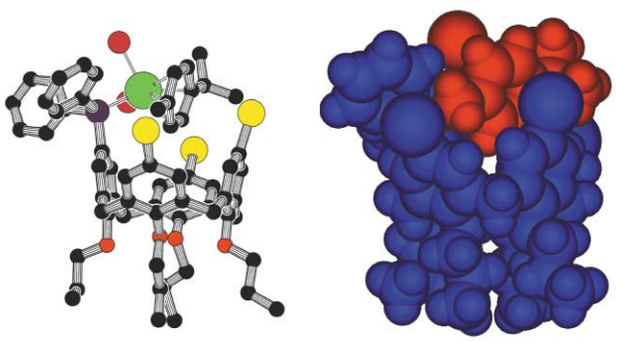


Fig. 4 Molecular structure of complex **17**: left, ball and stick representation; right, CPK model showing the enveloped "$RuCl_2$(*p*-cymene)" unit in red (CH_2Cl_2 and hexane solvates are not shown).

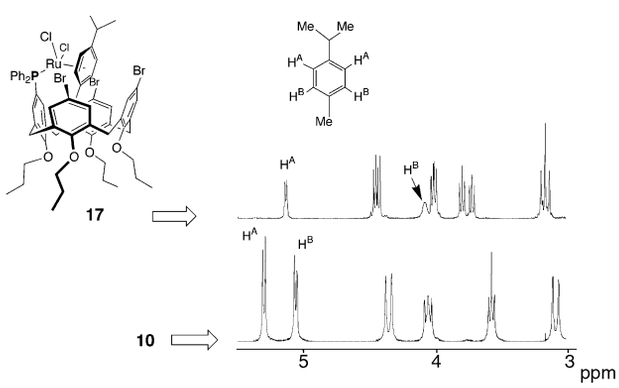
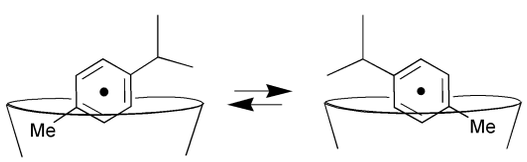


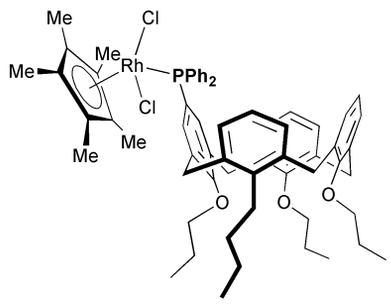
Fig. 5 ^{1}H NMR spectra ($CDCl_3$, partial view) of the ruthenium complexes **10** and **17**.

phenoxy rings, have undergone a highfield shift of *ca.* 1 ppm (!) when compared to the values found in **7**, **9** and **10** (Fig. 5). In contrast, the *meta*-H atoms and the Pr^i protons have normal chemical shifts (see Experimental), suggesting that the *p*-cymene ring undergoes restricted rotation about its coordination axis as shown in Scheme 3.



Scheme 3 Restricted rotation of the *p*-cymene unit about its coordination axis.

In the solid state, the Ar–Me bond of the *p*-cymene ligand is oriented sideways, pointing towards a bromine atom, thus probably minimizing steric interaction between the Ar–*Me* group and the two phenol rings that sandwich the *p*-cymene ring. Interestingly, in the related complex **18** where the calix cone is shorter, the coordinated $RhCp^*Cl_2$ unit ($Cp^* = C_5Me_5$) lies completely outside the cavity.[11] It is likely that for steric reasons the PPh rings of the bulky ligand **5** are oriented outwards, resulting in a phosphorus lone pair that points to the calix axis and which in turn forces metal complexation to occur at the cavity entrance. Overall the entrapment of the *p*-cymene unit may be regarded as a mechanical imprisonment within enlarged calixarene walls.



Conclusions

We have described a synthetic methodology that allows single or multiple phosphination at the upper-rim of calix[4]arenes. Multiple complexation was achieved with the di- and tetraphosphinated ligands resulting in complexes where the metal units are all maintained close to the upper rim. When behaving as chelators the 5,17-diphosphinated ligands **1** and **4** position the complexed metal centre exactly at the cone entrance. The fact that **1** and **4** may act as *cis*-chelators is rather unexpected in view of the high asymmetry generated in the resulting structures. Their dynamic behaviour in solution is probably a response to the steric strain induced in these calixarenes.

The most interesting feature of the "expanded" cavity **5** concerns the possibility to realize partial entrapment of coordinated metal units. Future work is aimed at exploiting this property for catalytic processes occurring inside a spatially-restricted environment.

Experimental

All manipulations involving phosphines were performed in Schlenk-type 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 and $^{31}P\{^1H\}$ spectra were recorded with FT Bruker instruments (AC-300 or Bruker AM-400). $^{13}C\{^1H\}$ were recorded with an FT Bruker AC-200 spectrometer. ^{1}H NMR spectra were referenced to residual protio solvents (7.26 ppm for $CDCl_3$ and 5.32 ppm for CD_2Cl_2), ^{13}C chemical shifts are reported relative to deuterated solvents (77.0 ppm for $CDCl_3$ and 53.8 ppm for CD_2Cl_2), and the ^{31}P NMR data are given relative to external H_3PO_4. Mass spectra were recorded on a ZAB HF VG analytical spectrometer using *m*-nitrobenzyl alcohol as matrix. Bu^tLi and Bu^nLi solutions were titrated according to a conventional method.[24] 5,11,17,23-Tetrabromo-25,26,27,28-tetrapropoxycalix[4]arene (**2**),[25] [AuCl(THT)],[26] [Pd(*o*-$C_6H_4CH_2NMe_2$)Cl]$_2$,[27] [$RuCl_2$(*p*-cymene)]$_2$,[28] [$PtCl_2$(COD)],[29] [$PtCl_2$(PhCN)$_2$],[30] [RhCl(norbornadiene)]$_2$,[31] [Pd(η^3-C_4H_7)Cl]$_2$,[32] were prepared according to methods reported in the literature. In the NMR data "C_q" denotes a quaternary carbon atom. In the following "dmba" stands for the *o*-$C_6H_4CH_2NMe_2$ ligand.

Syntheses

5,17-Bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene 1. To a cold (−78 °C) solution of **2** (2.169 g, 2.38 mmol) in THF (50 cm^3) was added a 1.72 M solution of Bu^tLi-pentane (2.8 cm^3, 4.8 mmol). After 1 h, Ph_2PCl (0.8 cm^3, 1.053 g, 4.76 mmol) was added dropwise and the solution was stirred for 10 h at −78 °C. The lithiation step was then repeated using the same amounts of Bu^tLi. The reaction was quenched with MeOH (3 cm^3). The solution was allowed to warm up to room temperature, evaporated to dryness and the residue was taken up with CH_2Cl_2. Addition of EtOH afforded a white precipitate. Yield: 1.875 g, 82%. mp > 280 °C. ^1H NMR ($CDCl_3$): δ 7.37–7.33 (20H, PPh_2), 7.06 [d, 4H, *m*-H of OArP, $^3J(PH)$ = 8 Hz], 6.29 and 6.11 (AB_2 spin system, 6H, *m* and *p*-H of OAr, ^3J = 8 Hz), 4.41 and 3.06 [2d, AB spin sytem, 8H, $ArCH_2Ar$, $^2J(AB)$ = 13.0 Hz], 4.03 (pseudo t, 4H, OCH_2, $^3J \approx 8$ Hz), 3.63 (t, 4H, OCH_2, ^3J = 8 Hz), 2.00 (m, 4H, OCH_2CH_2), 1.81 (m, 4H, OCH_2CH_2), 1.06 (t, 6H, CH_3, ^3J = 7.5 Hz), 0.91 (t, 6H, CH_3, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.80 and 155.10 (2s, arom. C_q–O), 137.25–122.02 (arom. C's), 77.00 and 76.60 (2s, OCH_2), 30.95 (s, $ArCH_2Ar$), 23.51 and 23.15 (2s, CH_2CH_3), 10.82 and 9.93 (2s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.4 (s, PPh_2). Found: C, 80.18; H, 6.74. Calc. for $C_{64}H_{66}O_4P_2$ (M_r = 961.18) C, 79.98; H, 6.92%.

5,11,17,23-Tetrakis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene 3. To a cold (−78 °C) solution of **2** (2.169 g, 2.38 mmol) in THF (50 cm^3) was added a 1.72 M solution of Bu^tLi–pentane (3.0 cm^3, 4.8 mmol). After 1 h, Ph_2PCl (0.8 cm^3, 1.053 g, 4.76 mmol) was added and the solution was stirred for 10 h at −78 °C. This lithiation/phosphination step was then repeated using the same amounts of Bu^tLi and Ph_2PCl. The solution was warmed up to room temperature, evaporated to dryness and the residue was taken up with CH_2Cl_2. Addition of EtOH afforded a white precipitate. Yield: 2.468 g, 78 %. mp > 280 °C. ^1H NMR ($CDCl_3$): δ 7.28–7.23 and 7.07–7.02 (40H, PPh_2), 6.74 [d, 8H, *m*-H of OArP, $^3J(PH)$ = 7.9 Hz], 4.41 and 3.05 [2d, AB spin system, 8H, $ArCH_2Ar$, $^2J(AB)$ = 13.0 Hz], 3.87 (t, 8H, OCH_2, ^3J = 8.0 Hz), 1.95 (m, 8H, OCH_2CH_2), 0.98 (t, 12H, CH_3, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.48 (s, arom. C_q–O), 135.03–124.73 (arom. C's), 76.47 (s, OCH_2), 31.31 (s, $ArCH_2Ar$), 23.15 (s, CH_2CH_3), 10.15 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.0 (s, PPh_2). Found: C,79.41; H, 6.53. Calc. for $C_{88}H_{84}O_4P_4$ (M_r = 1329.54) C, 79.50; H, 6.37%.

5,17-Dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene 4. To a solution of **2** (10.080 g, 11.1 mmol) in THF (50 cm^3) at −78 °C was added dropwise a 1.72 M solution of Bu^tLi–pentane (12.9 cm^3, 22.2 mmol). After 1 h, Ph_2PCl (3.8 cm^3, 22.2 mmol) was added and the solution was stirred for a further 10 h at −78 °C. The solvent was evaporated and the residue was taken up with $CHCl_3$. Addition of MeOH afforded a white precipitate. Yield: 7.9 g, 63%. mp 256 °C. ^1H NMR ($CDCl_3$): δ 7.51–7.37 (20H, PPh_2), 7.12 [d, 4H, *m*-H of OArP, $^3J(PH)$ = 7.5 Hz], 6.37 (s, 4H, *m*-H of OArBr), 4.40 and 3.07 [2d, AB spin system, 8H, $ArCH_2Ar$, $^2J(AB)$ = 13.3 Hz], 4.07 (t, OCH_2, ^3J = 8.0 Hz), 3.62 (t, 4H, OCH_2, ^3J = 6.7 Hz), 1.99 (m, 4H, OCH_2CH_2), 1.85 (m, 4H, OCH_2CH_2), 1.08 (t, 6H, CH_3, ^3J = 7.5 Hz), 0.92 (t, 6H, CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.40 and 154.27 (2s, C_q–O), 138.10–128.58 (arom. C's), 115.38 (s, CBr), 77.35 and 76.74 (2s, OCH_2), 30.85 (s, $ArCH_2Ar$), 23.43 and 23.08 (2s, CH_2CH_3), 10.77 and 9.79 (2s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.6 (s, PPh_2). Found: C, 68.45; H, 5.78. Calc. for $C_{64}H_{64}Br_2O_4P_2$ (M_r = 1118.98) C, 68.70; H, 5.77%.

5,11,17-Tribromo-23-diphenylphosphino-25,26,27,28-tetrapropoxycalix[4]arene 5. To a solution of **2** (5.010 g, 5.51 mmol) in THF (150 cm^3, −78 °C) was slowly added a 1.5 M solution of Bu^nLi–hexane (4.0 cm^3, 6.1 mmol). After 1 h, neat Ph_2PCl (1.0 cm^3, 5.5 mmol) was added and the solution was maintained at −78 °C for 10 h. The solution was then stirred for a further 5 h at room temperature. The solvent was removed and the residue was taken up with CH_2Cl_2. Addition of MeOH afforded a white precipitate which was purified by column chromatography (R_f = 0.3, SiO_2, CH_2Cl_2–hexane 80 : 20 v/v). Yield: 0.498 g, 10%. ^1H NMR ($CDCl_3$): δ 7.42–7.26 (m, 10H, PPh_2), 7.13 (s, 2H, *m*-H of OArBr), 6.90 [d, 2H, *m*-H of OArP, $^3J(PH)$ = 7.3 Hz], 6.62 and 6.53 [2d, AB spin system, 4H, *m*-H of OArBr, $^4J(AB)$ = 2.7 Hz], 4.40 and 3.11 [2d, AB spin system, 4H, $ArCH_2Ar$, $^2J(AB)$ = 13.8 Hz], 4.39 and 3.07 [2d, AB spin system, 4H, $ArCH_2Ar$, $^2J(AB)$ = 13.9 Hz], 3.99–3.92 (2 overlapped m, 6H, OCH_2 of OArP), 3.77–3.72 (2 overlapped t, 6H, OCH_2 of OArBr), 1.95–1.87 (m, 8H, OCH_2CH_2), 1.05, 0.97 and 0.95 (3 overlapped t, 12H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.69, 157.11 and 155.80 (3s, arom. C_q–O), 138.58–129.45 (arom. C's), 116.27 and 115.88 (2s, arom. C_q–Br), 78.11 (3 ×) and 77.75 (2s, OCH_2), 31.70 (s, $ArCH_2Ar$), 24.16 and 23.83 (2s, CH_2CH_3), 11.44, 10.98 and 10.88 (3s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.2 (s, PPh_2). Found: C, 61.47; H, 5.66. Calc. for $C_{52}H_{54}Br_3O_4P$ (M_r = 1013.67) C, 61.61; H, 5.37%.

Tetrachloro{5,11,17,23-tetra(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}gold(I) 6. A solution of [AuCl(tht)] (0.097 g, 0.30 mmol) in THF (1 cm^3) was added to a solution of **3** (0.100 g, 0.08 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 2 h the solution was filtered over Celite and the filtrate was concentrated to *ca.* 1 cm^3. Addition of hexane afforded the complex as a white powder. Yield: 0.120 g, 75%. mp 242–245 °C (dec.). ^1H NMR ($CDCl_3$): δ 7.62–7.55 and 7.45–7.37 (24H, PPh_2), 7.15, 7.11 and 7.00 (3d, 24H, arom. H's PPh_2 and calix), 4.51 and 3.20 [AB spin sytem, 8H, $ArCH_2Ar$, $^2J(AB)$ = 13 Hz], 3.99 (t, 8H, OCH_2, ^3J = 8 Hz), 1.98 (m, 8H, OCH_2CH_2), 1.02 (t, 12H, CH_3, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.45 (s, arom. C_q–O), 135.62–121.43 (arom. C's), 77.59 (s, OCH_2), 31.53 (s, $ArCH_2Ar$), 23.20 (s, CH_2CH_3), 10.23 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.12 (s, PPh_2). Found: C, 48.68; H, 3.95. Calc. for $C_{88}H_{84}Cl_4O_4P_4Au_4 \cdot C_6H_{14}$ (M_r = 2259.22 + 86.17) C, 48.14; H, 4.21%. This complex slowly decomposes in solution.

Tetra(dichloro)tetra(η^6-*p*-cymene)[5,11,23,17-tetra(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene]tetraruthenium(II) 7. A solution of $[RuCl_2(p\text{-cymene})]_2$ (0.050 g, 0.084 mmol) in CH_2Cl_2 (10 ml) was added to a solution of tetraphosphine **3** (0.056 g, 0.042 mmol) in CH_2Cl_2 (30 ml). After stirring for one night, the solution was evaporated to dryness and the residue was taken-up with $CHCl_3$. Addition of Et_2O afforded an orange precipitate. Yield: 0.076 g, 81%. mp 236 °C. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 7.49–7.00 (m, 48H, PPh_2 and *m*-H of calixarene), 5.29 and 5.05 [2d, AA′BB′ spin system, 16H, C_6H_4 of *p*-cymene $^3J(AB) = {}^3J(A'B')$ = 6.0 Hz], 4.48 and 3.19 [2d, AB spin system, 8H, $ArCH_2Ar$, $^2J(AB)$ = 12.9 Hz], 3.97 (t, 8H, OCH_2 of OArP, ^3J = 6.7 Hz), 2.6 [m, 4H, $CH(CH_3)_2$], 1.85 (m, 8H, OCH_2CH_2), 1.00 [d, 6H, $CH(CH_3)_2$, ^3J = 6.7 Hz], 0.91 (t, 12H, CH_3, ^3J = 7 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, 298 K, $CDCl_3$): δ 21.7 (s, PPh_2). Found: C, 59.93; H, 5.48. Calc. for $C_{128}H_{140}Cl_8O_4P_4Ru_4$ (M_r = 2554.33): C, 60.19; H, 5.52%.

Tetrachloro-tetra(*N*,*N*-dimethylaminobenzylamine){5,11,17,23-tetra(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}tetrapalladium(II) 8. A solution of $[Pd(o\text{-}C_6H_4NMe_2)Cl]_2$ (0.067 g, 0.12 mmol) in THF (1 cm^3) was added to a solution of the tetraphosphine **3** (0.080 g, 0.06 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 2 h the solution was filtered over Celite and the filtrate was concentrated to *ca.* 1 cm^3. Addition of pentane afforded the complex as a white precipitate. Yield: 0.120 g, 77%. mp 208–212 °C (dec.). ^1H NMR ($CDCl_3$): δ 7.43–7.20 (48H,

m-H of OAr and PPh_2), 6.25 and 5.97 (16H, arom H of dmba), 4.24 and 2.79 [AB spin sytem, 8H, $ArCH_2Ar$, ^2J(AB) = 13 Hz], 3.91(s, 8H, NCH_2 of dmba), 3.81 (t, 8H, OCH_2, ^3J = 7.8 Hz), 2.64 (d, 24H, NCH_3 of dmba, J = 2.1 Hz), 1.74 (m, 8H, OCH_2CH_2), 0.87 (t, 12H, CH_3, ^3J = 7.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.24 (s, arom. C_q–O), 152.32 and 148.44 (2s, C_q of dmba), 137.88–122.17 (arom. C's), 76.44 (s, OCH_2), 73.33 (s, NCH_2 of dmba), 50.39 (s, NCH_3 of dmba), 32.14 (s, $ArCH_2Ar$), 22.78 (s, CH_2CH_3), 10.24 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.27 (s, PPh_2). Found: C, 61.68; H, 5.46; N, 2.26. Calc. for $C_{124}H_{132}Cl_4N_4O_4P_4Pd_4$ (M_r = 2575.58): C, 61.20; H, 5.47; N, 2.30%.

Bis(dichloro)bis(η^6-*p*-cymene)[5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene]diruthenium(II) 9. A solution of $[RuCl_2(p\text{-cymene})]_2$ (0.096 g, 0.16 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of diphosphine **1** (0.150 g, 0.16 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of diethyl ether afforded an analytically pure orange powder. Yield: 0.165 g, 67%. mp 192–194 °C. ^1H NMR (CD_2Cl_2): δ 7.97–7.87 and 7.43–7.40 (m, 20H, PPh_2), 7.58 [d, 4H, *m*-ArH of OArP, ^3J(PH) = 10.4 Hz], 6.20 and 5.98 (d and t, AB_2 spin system, *m*-H and *p*-H of OAr, ^3J = 7.5 Hz), 5.25 and 5.11 [2d, AA′BB′ spin system, 8H, C_6H_4 of *p*-cymene ^3J(AB) = ^3J(A′B′) = 5.3 Hz], 4.37 and 3.08 (2d, AB spin system, 8H, $ArCH_2$, ^2J = 13.2 Hz), 4.05 (t, 4H, OCH_2 of OArP, ^3J = 6.9 Hz), 3.57 (t, 4H, OCH_2 of OArBr, ^3J = 6.7 Hz), 2.85 [hept., 2H, $CH(CH_3)_2$ of *p*-cymene], 1.95 (s, 6H, *p*-Me of *p*-cymene), 2.00–1.75 (2m, 8H, OCH_2CH_2), 1.13 [d, 6H, $CH(CH_3)_2$, ^3J = 6.9 Hz], 1.06 and 0.89 (2t, 12H, CH_3, ^3J = 7.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.09 and 154.94 (2s, arom. C_q–O), 136.89–122.25 (arom. C's), 110.50 and 95.89 (2s, arom. C_q's of *p*-cymene), 89.35 and 86.91 (2s, arom. CH of *p*-cymene), 77.70 and 77.07 (2s, OCH_2), 30.98 (s, $ArCH_2Ar$), 30.32 (s, $CH(CH_3)_2$), 23.51 and 23.18 (2s, CH_2CH_3), 17.86 (s, $ArCH_3$ of *p*-cymene), 10.88 and 9.85 (2s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.99 (s, PPh_2). Found: C, 64.14; H 6.23. Calc. for $C_{84}H_{94}Cl_4O_4P_2Ru_2$ (M_r = 1573.58): C, 64.12; H, 6.02%.

Bis(dichloro)bis(η^6-*p*-cymene)[5,17-(dibromo)-11,23-bis-(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene]-diruthenium(II) 10. A solution of $[RuCl_2(p\text{-cymene})]_2$ (0.030 g, 0.05 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of diphosphine **4** (0.056 g, 0.05 mmol) in CH_2Cl_2 (30 cm^3). After stirring for one night the solution was concentrated to *ca.* 5 cm^3. Addition of diethyl ether afforded an analytically pure orange powder. Yield: 0.081g, 90 %. mp 226–230 °C. ^1H NMR ($CDCl_3$): δ 7.95–7.89 and 7.50–7.41 (m, 20H, PPh_2), 7.55 [d, 4H, *m*-ArH of OArP, ^3J(PH) = 10.0 Hz], 6.24 (s, 4H, *m*-H of OArBr), 5.29 and 5.05 [2d, AA′BB′ spin system, 8H, C_6H_4 of *p*-cymene ^3J(AB) = ^3J(A′B′) = 6.0 Hz], 4.33 and 3.06 [2d, AB spin system, 8H, $ArCH_2Ar$, ^2J(AB) = 13.4 Hz], 4.04 (t, 4H, OCH_2 of OArP, ^3J = 8.3 Hz), 3.56 (t, 4H, OCH_2 of OArBr, ^3J = 6.7 Hz), 2.9 [m, 2H, $CH(CH_3)_2$ of *p*-cymene], 1.97 (s, 6H, *p*-Me of *p*-cymene), 1.95 and 1.80 (2m, 8H, OCH_2CH_2), 1.14 [d, 6H, $CH(CH_3)_2$, ^3J = 6.6 Hz], 1.05 and 0.88 (2t, 12H, CH_3, ^3J = 7.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.45 and 155.08 (2s, arom. C_q–O), 136.72–129.21 (arom. C's), 116.20 (s, arom. C_q–Br), 112.04 and 97.06 (2s, arom. C_q's of *p*-cymene), 89.65 and 88.47 (2s, arom. CH of *p*-cymene), 78.29 and 77.65 (2s, OCH_2), 31.82 [s, $CH(CH_3)_2$], 31.27 (s, $ArCH_2Ar$), 24.29 and 22.9 (2s, CH_2CH_3), 19.01 (s, $ArCH_3$ of *p*-cymene), 11.73 and 10.65 (2s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.08 (s, PPh_2). Found: C, 58.04; H, 5.00. Calc. for $C_{84}H_{92}Br_2Cl_4O_4P_2Ru_2$ (M_r = 1731.37): C, 58.27; H, 5.36%.

Dichloro-bis(*N*,*N*-dimethylaminobenzylamine){5,17-bis-(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}-dipalladium(II) 11. A solution of $[Pd(o\text{-}C_6H_4NMe_2)Cl]_2$ (0.075 g, 0.13 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of diphosphine **1** (0.130 g, 0.13 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 1 h the solution was concentrated to *ca.* 1 cm^3. Addition of hexane afforded complex **11** as a white precipitate. Yield: 0.150 g, 75%. mp 220–222 °C. ^1H NMR ($CDCl_3$): δ 7.81–7.7 and 7.45–7.37 (20H, PPh_2), 7.61 [d, 4H, *m*-ArH of OArP, ^3J(PH) = 11.6 Hz], 7.07–6.92 and 6.65–6.49 (8H, arom H of dmba), 6.05 and 5.64 (d and t, AB_2 spin system, 6H *m*-H and *p*-H of OAr, ^3J = 7.6 Hz), 4.39 and 3.04 [AB spin sytem, 8H, $ArCH_2Ar$, ^2J(AB) = 13.4 Hz], 4.05 (t, 4H, OCH_2, ^3J = 7.5 Hz), 4.04 [d, 4H, NCH_2 of dmba, ^4J(PH) = 2 Hz], 3.57 (t, 4H, OCH_2, ^3J = 6.6 Hz), 2.90 (d, 12H, NCH_3 of dmba, ^4J = 2.4 Hz), 2.02–1.77 (m, 8H, OCH_2CH_2), 1.08 and 0.93 (2t, 12H, CH_3, ^3J = 7.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.51 and 154.91 (2s, arom. C_q–O), 151.4 and 148.1 (2s, C_q of dmba), 136.37–122.42 (arom. C's), 77.35 and 76.50 (2s, OCH_2), 73.25 (s, NCH_2), 50.52 (s, NCH_3), 31.00 (s, $ArCH_2Ar$), 23.55 and 23.18 (2s, CH_2CH_3), 10.85 and 9.86 (2s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.62 (s, PPh_2). Found: C, 65.77; H, 5.68. Calc. for $C_{82}H_{90}Cl_2N_2O_4P_2Pd_2$ (M_r = 1513.30): C, 65.08; H, 5.68%.

***cis*-*P*,*P*′-Dichloro{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}platinum(II) 12.** A solution of diphosphine **4** (0.167 g, 0.15 mmol) in CH_2Cl_2 (250 cm^3) and a solution of $[PtCl_2(COD)]$ (0.056 g, 0.15 mmol) in CH_2Cl_2 (250 cm^3) were added simultaneously into a 2 L flask contaning 750 cm^3 of CH_2Cl_2 over a period of 4 h. The resulting solution was stirred overnight at room temperature. The solution was concentrated to *ca.* 5 cm^3. Addition of toluene afforded a white precipitate. Yield: 0.183 g, 90%. mp > 280 °C. ^1H NMR ($CDCl_3$): consistent with the formation of a monomer, all signals are sharp: δ 7.28–7.03 (m, 24 H, PPh_2 and *m*-H of OArP), 6.91 (broad s, 4H, *m*-H of OArBr), 4.49 and 3.21 [2d, AB spin system, 8H, $ArCH_2$ Ar, ^3J(AB) = 13.7 Hz], 4.08 (t, 4H, OCH_2 of OArP, ^3J = 8.1 Hz), 3.80 (t, 4H, OCH_2 of OArBr, ^3J = 6.3 Hz), 1.95–1.88 (m, 8H, OCH_2 CH_2), 1.16 and 0.89 (2t, 12H, CH_3, ^3J = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.87 and 156.56 (2s, arom. C_q–O), 138.40–125.36 (arom. C's), 116.32 (s, arom. C_q–Br), 77.42 and 77.08 (2s, OCH_2), 31.13 (s, $ArCH_2Ar$), 23.63 and 22.78 (2s, CH_2CH_3), 10.89 and 9.77 (2s, CH_3). $^{31}P\{^1H\}$ ($CDCl_3$): δ 11.2 [s with Pt satellites, PPh_2, J(PPt) = 3621 Hz]. FAB mass spectrum: *m*/*z* (%) 1349.2 (100) [M − Cl]$^+$, 1313.1 (62) [M − 2Cl]$^+$. Found: C, 54.29; H, 4.82. Calc. for $C_{64}H_{64}Br_2Cl_2O_4P_2Pt{\cdot}0.5CH_2Cl_2$ (M_r = 1384.97 + 42.47): C, 54.27; H, 4.59%.

Oligomer [PtCl$_2$·4]$_n$. A solution of $[PtCl_2(COD)]$ (0.078 g, 0.20 mmol) in CH_2Cl_2 (5 cm^3) was added to a stirred solution of **4** (0.220 g, 0.20 mmol) in CH_2Cl_2 (5 cm^3). After stirring overnight, the solution was concentrated to *ca.* 2 cm^3 and addition of diethyl ether afforded a white precipitate. Yield: 0.195 g, 95%. mp > 280 °C. ^1H NMR (400 MHz, 388 K, $C_2D_2Cl_4$): the following signals are typically broad for an oligomer: δ 7.70–7.65 and 7.45–7.38 (2m, 24H, PPh_2 and *m*-H of OArP), 6.14 (s, 4H, *m*-H of OArBr), 4.37 and 3.03 [2d, AB spin system, 8H, $ArCH_2Ar$, ^2J(AB) = 13.4 Hz], 4.12 (t, 4H, OCH_2 of OArP, ^3J = 7.1 Hz), 3.68 (t, 4H, OCH_2 of OArBr, ^3J = 5.6 Hz), 1.93–1.85 (m, 8H, OCH_2CH_2), 1.12 and 0.95 (2t, 12H, CH_3, ^3J = 7.3 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 160.87 and 154.86 (2s, arom. C_q–O), 136.86–128.66 (arom. C's), 115.61 (s, arom. C_q–Br), 77.98 and 77.31 (2s, OCH_2), 31.26 (s, $ArCH_2Ar$), 23.83 and 23.52 (2s, CH_2CH_3), 11.09 and 9.95 (2s, CH_3). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 13.7 [s with Pt satellites, PPh_2, J(PPt) = 3660 Hz]. Molecular weight determination by osmometry (CH_2Cl_2): 14000 ± 90, corresponding to a formal value of n = 10. FAB mass spectrum: *m*/*z* (%) 1349.5 (10) [M − Cl], 1312.7 (100) [M − 2Cl]. Found: C, 55.60; H, 4.41. Calc. for $[C_{64}H_{64}Br_2Cl_2O_4P_2Pt]_n$ (M_r = n × 1384.97): C, 55.60; H, 4.66%.

***cis*-*P*,*P*′-Dichloro{5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}platinum(II) 13.** A solution of

diphosphine **1** (0.150 g, 0.16 mmol) in CH_2Cl_2 (250 cm^3) and a solution of [$PtCl_2$(COD)] (0.059 g, 0.16 mmol) in CH_2Cl_2 (250 cm^3) were added simultaneously into a 2 L flask containing 750 cm^3 of CH_2Cl_2 over a period of 4 h. The resulting solution was stirred for 15 h at room temperature. The solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded **13** as a white precipitate. Yield: 0.172 g, 90%. mp > 280 °C. ^{1}H NMR ($CDCl_3$): all signals are sharp: δ 7.26–6.98 (m, 24 H, PPh_2 and *m*-H of OArP), 6.88 (broad s, 4H, *m*-H of OAr), 4.56 and 3.26 [2d, AB spin system, 8H, ArCH_2Ar, ^3J(AB) = 13.7 Hz], 4.10 (t, 4H, OCH_2 of OArP, ^3J = 7.8 Hz), 3.82 (t, 4H, OCH_2 of OAr, ^3J = 6.3 Hz), 1.96–1.91 (m, 8H, OCH_2CH_2), 1.17 and 0.89 (2t, 12H, CH_3, ^3J = 7.3 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.10 and 157.31 (2s, arom. C_q–O), 136.49–123.94 (arom. C's), 77.50 and 77.05 (2s, OCH_2), 31.28 (s, ArCH_2Ar), 23.63 and 22.84 (2s, CH_2CH_3), 10.91 and 9.81 (2s, CH_3). ^{31}P{^{1}H}NMR ($CDCl_3$): δ 10.4 [s with Pt satellites, PPh_2, J(PPt) = 3651 Hz]. FAB mass spectrum: *m*/*z* (%) 1226.3 (15) [M^+, expected isotopic profile)], 1191.3 (100) [$(M - Cl)^+$], 1155.3 (62) [$(M - 2Cl)^+$]. Found: C, 62.50; H, 5.37. Calc. for $C_{64}H_{66}Cl_2O_4P_2Pt$ (M_r = 1227.18): C, 62,64; H, 5.42%.

***trans*-*P*,*P*′-Dichloro{5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}platinum(II) 14.** A solution of [$PtCl_2$(PhCN)] (0.074 g, 0.16 mmol) in CH_2Cl_2 (150 cm^3) was added dropwise to a solution of **1** (0.150 mg, 0.16 mmol) in CH_2Cl_2 (800 cm^3) within 1 h. The resulting solution was stirred overnight at room temperature. The solution was concentrated to *ca.* 5 cm^3 and addition of hexane afforded a yellow precipitate. Yield: 0.086 g, 45%. mp > 250 °C. ^{1}H NMR ($CDCl_3$): all signals are sharp, in keeping with a monomeric structure: δ 7.75–7.72 and 7.28–7.27 (2m, 20 H, PPh_2), 6.85 and 6.70 (d and t, AB_2 spin system, 6H *m*-H and *p*-H of OAr, ^3J = 7.5 Hz), 6.74 [virtual t, 4H, *m*-H of OArP, ^{3+5}J(PH) = 10.5 Hz], 4.48 and 3.14 [2d, AB spin system, 8H, ArCH_2Ar, ^3J(AB) = 13 Hz], 4.07 (t, 4H, OCH_2 of OArP, ^3J = 8.3 Hz), 3.77 (t, 4H, OCH_2 of OArBr, ^3J = 6.9 Hz), 2.11–1.92 (2m, 8H, OCH_2CH_2), 1.14 and 0.91 (2t, 12H, CH_3, ^3J = 7.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.02 and 156.33 (2s, arom. C_q–O), 133.35–122.00 (arom. C's), 77.42 and 76.42 (2s, OCH_2), 30.80 (s, ArCH_2Ar), 23.61 and 23.01 (2s, CH_2CH_3), 10.83 and 9.82 (2s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.6 [s with Pt satellites, PPh_2, J(PPt) = 2584 Hz]. FAB mass spectrum: *m*/*z* (%) 1191.2 (38) [$(M - Cl)^+$, expected istopic profile], 1170.3 (47) [$(M - Cl + O)^+$, expected isotopic profile], 1155.3 (100) [$(M - 2Cl)^+$, expected isotopic profile] (the assignment of a monomeric structure is based on the sharpness of the NMR signals). Found: C, 62.49; H, 5.63. Calc. for $C_{64}H_{66}Cl_2O_4P_2Pt$ (M_r = 1227.18): C, 62.64; H, 5.42%.

***cis*-*P*,*P*′-{[5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene]norbornadiene}rhodium(I) tetrafluoroborate 15.** A solution of $AgBF_4$ (0.031 g, 0.16 mmol) in THF (1 cm^3) was added to a solution of [{RhCl(norbornadiene)}$_2$] (0.036 g, 0.08 mmol) in CH_2Cl_2 (10 cm^3). Stirring was stopped after 5 min and the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **1** (0.150 g, 0.16 mmol) in CH_2Cl_2 at −40 °C (30 cm^3). After 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of hexane afforded an orange precipitate. Yield: 0.049 g, 25%. mp 227 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 7.22–6.76 (m, 24H, PPh_2 and *m*-H of OArBr), 6.50 [virtual t, 4H, *m*-H of OArP, ^{3+5}J(PH) = 10 Hz], 4.57 and 3.25 [2d, AB spin system, 8H, ArCH_2Ar, ^3J(AB) = 13.9 Hz], 4.37 (broad s, 4H, =CH of nbd), 4.08 (t, 4H, OCH_2 of OArP, ^3J = 8.3 Hz), 3.91 (broad s, 2H, CH_2 of nbd), 3.79 (t, 4H, OCH_2 of OArBr, ^3J = 6.3 Hz), 1.94–1.87 (m, 8H, OCH_2CH_2), 1.42 (broad s, 2H, CH of nbd), 1.14 and 0.84 (2t, 12H, CH_3, ^3J = 7.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.19 and 158.17 (2s, arom. C_q–O), 136.99–122.31 (arom. C's), 77.34 and 76.71 (2s, OCH_2), 52.70 (CH of nbd), 30.92 (s, ArCH_2Ar), 29.72 (CH_2 of nbd), 23.61 and 22.76 (2s, CH_2CH_3), 10.87 and 9.70 (2s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 24.6 [d, PPh_2, J(PRh) = 156 Hz]. FAB mass spectrum: *m*/*z* (%) 1258.4 (3) [$M - O]^+$, 1171.5 (43) [$M - BF_4 + O]^+$, 1155.55 (38) [$M - BF_4]^+$. Found: C, 68.83; H, 6.19. Calc. for $C_{71}H_{74}BF_4O_4P_2Rh$ (M_r = 1243.04): C, 68.61; H, 6.00%.

(η^3-2-Methylallyl){*P*,*P*′-[5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene]}palladium(II) tetrafluoroborate 16. A solution of $AgBF_4$ (0.020 g, 0.10 mmol) in THF (1 cm^3) was added to a solution of [Pd(η^3-C_4H_7)Cl]$_2$ (0.020 g, 0.05 mmol) in CH_2Cl_2(3 cm^3). Stirring was stopped after 5 min and the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of diphosphine **1** (0.100 g, 0.104 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a white precipitate. Yield: 0.113 g, 90%. mp > 280 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.36–6.34 (30H, aromatic H), 4.56 and 3.25 [d, AB spin system, 4H, ArCH_2Ar, ^3J(AB) = 14.1 Hz], 4.55 and 3.23 [d, AB spin system, 4H, ArCH_2Ar, ^3J(AB) = 14.0 Hz], 4.12–4.05 (m, 4H, OCH_2 of OArP), 3.83 (t, 4H, OCH_2 of OArBr, ^3J = 5.7 Hz), 3.51 (broad s, 2H, CH_{syn}-allyl), 3.09–3.03 (broad m, 2H, CH_{anti}-allyl), 2.06 (s, 3H, Me-allyl), 1.99–1.87 (m, 8H, OCH_2CH_2), 1.19 (t, 6H, CH_2CH_3, ^3J = 7.3 Hz), 0.88–0.85 (2 overlapping t, 6H, CH_2-CH_3). Running the ^{1}H NMR spectrum at 223 K on a 500 MHz spectrum splits all signals, resulting in a C_1-symmetrical species. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, 121 MHz): δ 23.11 (s, PPh_2). ^{31}P{^{1}H}NMR (CD_2Cl_2, 223 K, 202 MHz): δ 24.4 and 24.0 [AB spin system, J(AB) = 37 Hz]. FAB mass spectrum: *m*/*z* (%) 1121.3 (100) [$(M - BF_4)^+$, expected isotopic profile], 1066.2 (20) [$(M - Cl)^+$, expected isotopic profile). Found: C, 67.71; H, 6.09. Calc. for $C_{68}H_{73}BF_4O_4P_2Pd$ (M_r = 1209.49): C, 67.53; H, 6.08%.

Dichloro(η^6-*p*-cymene)[5-diphenylphosphino-11,17,23-tribromo-25,26,27,28-tetrapropoxycalix[4]arene]ruthenium(II) 17. A solution of [$RuCl_2$(*p*-cymene)]$_2$ (0.034 g, 0.056 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to a solution of monophosphine **5** (0.113 g, 0.112 mmol) in CH_2Cl_2 (50 cm^3). After stirring for 15 min the solution was concentrated to *ca.* 5 cm^3. Addition of hexane afforded **17** as an analytically pure orange powder. Yield: 0.125 g, 85%. mp 163 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.56–7.26 (10H, PPh_2), 7.12 [d, 2H, *m*-H of OArP, ^3J(PH) = 5 Hz], (s, 2H, *m*-H of OArBr), 7.10 and 7.00 [2d, AB spin system, 4H, *m*-H of OArBr, ^4J(AB) = 2 Hz], 6.74 (s, 2H, *m*-H of OArBr), 5.13 and 4.10 [2d, AA′BB′ spin system, 8H, C_6H_4 of *p*-cymene, ^3J(AB) = ^3J(A′B′) = 6 Hz], 4.47 and 3.21 [2d, AB spin system, 4H, ArCH_2Ar, ^2J(AB) = 13 Hz], 4.41 and 3.14 [2d, AB spin system, 4H, ArCH_2Ar, ^2J(AB) = 12 Hz], 4.06–3.97 (m, 4H, OCH_2 of OArBr), 3.80–3.72 [5H, OCH_2 and CH(CH_3)$_2$ of *p*-cymene], 2.12–1.86 (m, 8H, OCH_2CH_2), 1.25 [d, 6H, CH(CH_3)$_2$], 1.07, 1.00, and 0.96 (3 overlapping t, 3H : 6H : 3H, CH_3), 1.03 (s, 3H, *p*-Me of *p*-cymene). As shown by a 2D ROESY experiment, the Ar*Me* protons correlate with the *m*-H at 6.74 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 27.4 (s, PPh_2). Found: C, 54.72; H, 5.18. Calc. for $C_{62}H_{68}Br_3Cl_2O_4PRu\cdot 1/2CH_2Cl_2$ (M_r = 1319.89 + 42.46): C, 55.10; H, 5.11%.

X-Ray crystallography

Crystal data for 12. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a chloroform solution: $C_{64}H_{64}Br_2Cl_2O_4P_2Pt\cdot 2CHCl_3$, M = 1623.74, triclinic, space group $P\bar{1}$, colourless prisms, a = 14.9754(2), b = 15.6505(2), c = 16.3093(2) Å, α = 67.133(5), β = 69.265(5), γ = 83.969(5)°, U = 3291.59(7) Å^3, Z = 2, μ = 0.377 mm^{-1}, F(000) = 1616. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, 0.71073 Å) at −100 °C. 21721 Reflections collected with 2.5 < θ < 27.50°, 12196 data with I > 3σ(I). The structure was solved by direct methods and refined anisotropically on F^2 using the OpenMoleN package.[33]

Hydrogen atoms were included using a riding model or rigid methyl groups. Final results: $R(F) = 0.031$, $wR(F) = 0.043$, goodness-of-fit = 1.012, 748 parameters, largest difference peak = 1.181 e Å^{-3}.

CCDC reference number 174550.

Crystal data for 16. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a chloroform solution of the complex: $C_{68}H_{73}BF_4O_4P_2Pd\cdot CHCl_3$, M = 1328.87, tetragonal space group, $P4/n$, pale yellow, a = 34.292(5), b = 34.292(5), c = 11.204(5) Å, U = 13175(6) Å^3, D_c = 1.272, Z = 8, μ = 0.447 mm^{-1}, $F(000)$ = 5212. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, 0.71073 Å) at −100 °C. 18836 Reflections collected with $1.88 < \theta < 30.03°$, 9230 data with $I > 2\sigma(I)$. The structure was solved by direct methods and refined anisotropically on F^2 using the SHELXL-97 procedure.[34] Hydrogen atoms were included using a riding model or rigid methyl groups. The chloroform molecule is disordered over two positions. There is also some disorder in one propyl group. Final results: $R(F^2) = 0.073$, $wR(F^2) = 0.21$, goodness-of-fit = 1.013, 734 parameters, largest difference peak = 2.1 e Å^{-3}.

CCDC reference number 174549.

Crystal data for 17. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of the complex: $C_{62}H_{68}Br_3Cl_2O_4PRu\cdot 3CH_2Cl_2\cdot$ 0.5hexane, M = 1617.80, triclinic, space group $P\bar{1}$, orange–red crystals, a = 11.7406(3), b = 15.2248(4), c = 21.8972(5) Å, α = 77.445(5), β = 88.005(5), γ = 73.474(5)°, U = 3661.2(2) Å^3, Z = 2, μ = 0.221 mm^{-1}, $F(000)$ = 1642. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, 0.71073 Å) at −100 °C. 21030 Reflections collected with $2.5 < \theta < 27.48°$, 7201 data with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically on F^2 using the OpenMoleN package.[33] Hydrogen atoms were included using a riding model or rigid methyl groups. One dichloromethane molecule is disordered over two positions. Final results: $R(F) = 0.060$, $wR(F) = 0.085$, goodness-of-fit = 1.382, 732 parameters, largest difference peak = 1.059 e Å^{-3}.

CCDC reference number 174551.

See http://www.rsc.org/suppdata/dt/b1/b110884k/ for crystallographic data in CIF or other electronic format.

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