# Upper-rim monofunctionalization of calix[4]arene by organometallic diphenylphosphinorhodium complexes†

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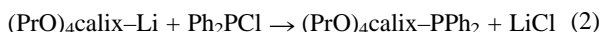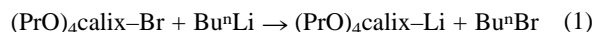
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**Monofunctionalization of the calix[4]arene upper-rim is achieved by lithiation with $Bu^nLi$, followed by phosphination with $Ph_2PCl$ of monobromotetra-*n*-propoxycalix[4]arene; subsequent reactions with $[Cp*Rh^{III}Cl_2]_2$ and $Cp*Rh^I(CO)_2$ provide the corresponding $Cp*[Ph_2(calix)P]Rh^{III}Cl_2$, which can be converted to $Cp*[Ph_2(calix)P]Rh^{III}(H)_2$ and $Cp*[Ph_2(calix)P]Rh^I(CO)$, respectively.**

Substituted derivatives of the bowl-like calix[4]arene are easy to synthesize and extremely rich chemistry has emerged from this simple molecule, primarily due to the pioneering work of Gutsche.[1] Many applications in the area of cation binding and transport are now known, and highly selective receptors and novel sensors for polyanionic species have been discovered with this host.[2] Recently, several researchers have prepared transition metal complexes of this platform molecule, mainly *via* the lower-rim section,[3] but some rare upper-rim functionalizations have also appeared in the literature.[4] Of particular interest, Matt and coworkers synthesized conic calix[4]arene complexes using two anchoring phosphine groups placed opposite to each other in the upper-rim.[5] Complexation induced a loop structure where the calix[4]arene cavity was blocked by the transition metal fragment, hence, losing its important hydrophobic hosting function. We now report the first monofunctionalization of the calix[4]arene upper-rim, using the $Ph_2P$ complexing fragment, along with some of its Rh complexes. The complexation of an Rh residue near a hosting device offers the hope of convenient regioselective reactivity in situations where the reacting molecule reversibly binds the calix[4]arene cavity. Many Cp*Rh complexes are known to activate C–H bonds,[6] and anchoring this fragment onto the supramolecular calix[4]arene represents a unique opportunity of potential regioselective C–H bond activation. This work describes the syntheses and characterization of three ($\eta^5$-pentamethylcyclopentadienyl)rhodium complexes of diphenylphosphinocalix-[4]arene.

The entry into the monofunctionalization proceeds *via* the use of the known monobromotetra-*n*-propoxycalix[4]arene **1**.[7] In this case, simultaneous standard lithiation and phosphination procedures produce the monophosphine ligand: [eqn. (1) and (2)].

$$(PrO)_4calix–Br + Bu^nLi \rightarrow (PrO)_4calix–Li + Bu^nBr \quad (1)$$

$$(PrO)_4calix–Li + Ph_2PCl \rightarrow (PrO)_4calix–PPh_2 + LiCl \quad (2)$$

The latter is easily oxidized to its oxo form in the presence of air in solutions as evidenced from the X-ray structure determination to be described elsewhere, and therefore inert conditions must be used at all times.

The complexation routes of **2** with Cp*Rh complexes are shown in Scheme 1. Complex **3** is conveniently synthesized by directly reacting the known dimeric $[Cp*RhCl_2]_2$[8] with **2**, and is obtained in 85% isolated yield. Complex **3** is relatively stable

† Electronic supplementary information (ESI) available: synthesis and characterisation of compounds **2**–**5**. See http://www.rsc.org/suppdata/cc/b0/b001485k/

and has been structurally characterized by X-ray methods.‡ Fig. 1 shows the X-ray structure and confirms the expected monofunctionalization of the calix[4]arene. The coordination environment of the $Rh^{III}$ metal center is relatively similar to that
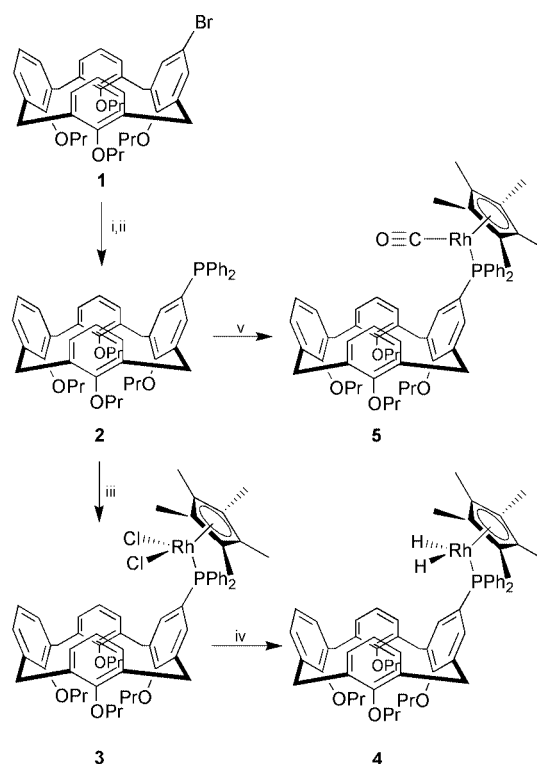
**Scheme 1** Synthesis of **2**–**5**. *Reagents and conditions*: i, BuLi/THF/−78 °C; ii, ClPPh$_2$/THF/−78 °C; *iii*, $[Cp*RhCl_2]_2$/EtOH/reflux 5 h; *iv*, NaBH$_4$/EtOH/reflux 1 h; v, Cp*Rh(CO)$_2$/benzene/reflux 24 h.
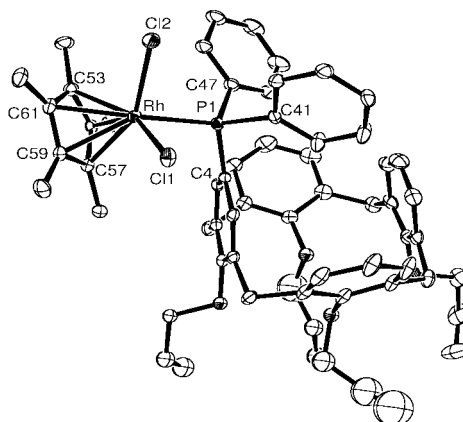
**Fig. 1** ORTEP drawing of **3**. Ellipsoids are shown at 10% probability and H atoms are not shown for clarity. Selected bond and distances (Å) and angles (°): Rh–C11 2.3835(18), Rh–C12 2.4053(20), Rh–P 2.3354(18), av. Rh–Cl 2.19(3); C11–Rh–C12 93.54(8), C11–Rh–P 85.71(6), P–Rh–C12 93.50(7).

of the reported less encumbered [Cp*Rh(Cl)$_2$P(Me)$_2$CH$_2$]$_2$ complex.[9]

The key feature of this structure is that **3** exhibits calix C–P and P–Rh single bonds and at least 12 conformations are possible. Rotation around this C–P bond provides two rotamers where part of the cavity opening is covered by phenyl groups, and one where the metallic residue occupies this specific above position ($C_s$ point group). The single crystal data shows one of the former described rotamers (Ph group on top of the cavity), and the Cp*RhCl$_2$ fragment adopts a conformation exhibiting a minimum of steric hindrance between Cp* and Ph, as shown in Fig. 1. $^1$H NMR spectroscopy clearly established the presence of fluxionality in **3**. Between 218 and 343 K, the spectra exhibit three main regions including the aromatic, methylene and propyl $^1$H region, which all undergo coalescence processes. The most striking observation is that both the PPh$_2$ proton and aromatic signals coalesce at the same temperature of *ca.* 268 K, corresponding to $\cong$ 2.2 kJ mol$^{-1}$. This result strongly indicates that the fluxion must involve cooperative motions of the Ph groups and the calix[4]arene aromatic fragments. The most probable motion is rotation of the Cp*(PPh$_2$)RhCl$_2$ group around the calix C–P single bond, where the Ph groups also rotate to pass over the bowlic structure of the calix[4]arene residue. Computer modellings clearly demonstrate that indeed rotations around the calix C–P bond must be accompanied by cooperative rotations of the Ph–P bond, somewhat similar to a 'merry-go-round' motion, allowing the Ph substituents to hop over the calix[4]arene 'walls'.

Complex **3** predictably reacts with NaBH$_4$ in refluxing ethanol to produce the corresponding dihydride **4**. The latter is very reactive, particularly in the presence of light and air, and must be freshly prepared prior to further studies. The presence of hydride groups in **4** is readily illustrated from its $^1$H NMR and IR spectra which exhibit a characteristic resonance at $\delta$ –13.07 ($^1J_{HRh}$ = 28 Hz, $^1J_{HP}$ = 38 Hz ), and an absorption at 2080 cm$^{-1}$ ($\nu_{RhH}$), respectively. Complexation of monophosphine ligand **2** can also be performed with the mononuclear Cp*Rh$^I$(CO)$_2$ complex[10] *via* a simple thermally induced CO substitution, to form **5**. A single and characteristic $\nu_{CO}$ absorption is indeed observed at 1960 cm$^{-1}$ in the solid state, and a complete characterization by standard methods (NMR, FAB mass, chemical analysis), confirms the identity and purity of this novel complex. Complex **5** is somewhat more stable than the dihydride **4**, but decomposition can also be observed upon UV–VIS light irradiation. Preliminary results show that indeed both **4** and **5** either thermally or photochemically eliminate H$_2$ and CO, respectively, to generate the very reactive species Cp*RhL (L = phosphine ligand, here **2**).[11] This important intermediate postulated as Cp*Rh[Ph$_2$P(calix)], is anticipated to activate C–H bonds,[12] and regioselectivity would be an unprecedented asset. Preparation of the more basic and less encumbered R$_2$P–calix ligand (R = Pr$^i$) and its Cp*Rh complex

has been successful. Their structural properties and reactivities are under investigation, and will be published in due course.

## Notes and references

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