



Calix[4]arene bisphosphite ligands bearing two distal 2,2'-biphenyldioxy or 2,2'-binaphthyldioxy moieties: conformational flexibility and allyl–palladium complexes

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ABSTRACT

Achiral and chiral calix[4]arene bisphosphite ligands (**2** and **3**) bearing two distal 2,2'-biphenyldioxyphosphinoxy and 2,2'-binaphthyldioxyphosphinoxy moieties, respectively, have been synthesized. Each of these ligands exists in two pairs of interconverting conformations in solution. The partial cone conformer (A) of the (bis)biphenyldioxyphosphinoxy ligand **2** has been separated by fractional crystallization and its structure established by X-ray crystallography. The mechanism of interconversion of the pairs of conformers (A/B and C/D) has been probed by two-dimensional NMR spectroscopy. The ¹H and ³¹P NMR evidence strongly supports a similar kind of exchange mechanism for ligand **3**. Freezing of the cone conformer from the interconverting C/D pair of conformers of ligand **2** has been achieved by complexation with (allyl)palladium moieties. The methyl–allyl complex (**2d**) is moderately effective for catalytic regioselective allylic alkylation of crotyl acetate.

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1. Introduction

Calixarenes, in particular calix[4]arenes, and allyl–palladium complexes have engendered considerable interest in the field of supramolecular chemistry and organometallic chemistry, respectively. There has been no significant attempt to combine these two chemically and structurally diverse areas of chemistry. Only a few examples of allyl–palladium complexes of conformationally rigid phosphorus functionalized calix[4]arenes are known,¹ but a detailed and combined study of the solution and solid-state structures of phosphorus functionalized calix[4]arenes and their allyl–palladium complexes is lacking.

Calix[4]arenes can exist in four different conformations, viz., cone, partial cone, 1,3-alternate, 1,2-alternate, and this feature provides a convenient handle for modifying the properties of calix[4]arenes.² 5,11,17,23-Tetra-(*p*-*tert*-butyl)-25,26,27,28-tetramethoxycalix[4]arene^{3a–d} and upper rim calix-crowns^{3e} have been used as model systems to study the mechanism of interconversion among the different conformations of calixarenes in solution. Matt and co-workers have reported the isolation of two isomers (cone and 1,2-alternate conformers) of 5,11,17,23-tetra-(*tert*-butyl)-25,27-bis(diphenylphosphinoxy)-

26,28-dimethoxycalix[4]arene and their dynamic behavior in solution by variable temperature ¹H NMR measurements.⁴ More recently, they have reported the synthesis, structure, and catalytic activity of a conformationally rigid calix[4]arene dipropoxy bisphosphite bearing 2,2'-binaphthyldioxyphosphinoxy moieties.⁵ Schmutzler, Borner and their co-workers have reported a calix[4]arene bisphosphite and a bisphosphonite bearing the methoxy and *tert*-butyl substituted biphenyldioxy or biphenylmonoxy moieties, respectively, and demonstrated the utility of the Rh(I) complexes of these calixarene phosphorus derivatives as catalysts for hydroformylation of 1-octene.⁶ In this paper, we wish to report the synthesis of semi-flexible 26,28-dimethoxycalix[4]arene bisphosphite ligands (**2** and **3**) bearing two distal 2,2'-biphenyldioxyphosphinoxy or 2,2'-binaphthyldioxyphosphinoxy moieties, which exist as two pairs of mutually interconverting conformers. We have probed the mechanism of conformational interconversion with the help of two-dimensional NMR spectroscopy. We have been able to freeze a particular conformer from the mixture of two thermodynamically stable and interconverting conformers by complexation with (allyl)palladium moieties. The conformations of the calix[4]arene framework as well as the regiochemistry of the allyl ligands in these complexes in solution and solid-state have been investigated. Preliminary accounts of our work reported here have been presented in two National Conferences.⁷

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2. Results and discussion

2.1. Synthesis and 2D NMR study of conformational interconversion of ligand 2

When a suspension of 1,3-dimethoxy-*p-tert*-butyl-calix[4]arene (**1**),⁸ in toluene, is treated with [1,1'-biphenyl]-2,2'-phosphorochloridite in the presence of NaH, the biphenyldioxyphosphino calix[4]arene derivative (**2**) is obtained in 27% yield (Scheme 1). This compound exists as a mixture of four conformers (A, B, C, and D). Fractional crystallization of the mixture from CHCl₃–hexane gave single crystals of conformer (A), leaving behind the conformers (C) and (D) in the mother liquor with a trace amount of the mixture of (A) and (B) (Scheme 2). When the solid sample of conformer (A) is dissolved in CDCl₃, the solution shows the presence of two interconverting conformers (A) and (B) as revealed by its ¹H and ³¹P NMR spectra. Two singlets at δ 121.1 and 134.7 are assigned to the partial cone conformer (A) with a C_s point group symmetry; the singlet at δ 139.5 is assigned to 1,2-alternate conformer (B), which has a center of symmetry at the mid point of the plane of the methylene bridge carbon atoms [point group C_i] (Scheme 2). The ¹H NMR spectral data (eight doublets for methylene bridge protons and two singlets for methoxy protons) are also consistent with the presence of two conformers (see Section 4). The structure of the partial cone conformer (A) has been established by X-ray crystallography (see later). For the other pair of conformers (C/D), left behind in the mother liquor after the isolation of A, the ¹H NMR spectrum shows two doublets at δ 4.48 and 3.24 ($\Delta\delta=1.24$) for the methylene bridge protons typical of cone conformation (C). Four doublets for the –CH₂– protons and two singlets (δ 3.12 and 3.47) for the two non-equivalent –OCH₃ protons are observed for the partial cone conformer (D). One singlet at δ 37.77 in the ¹³C NMR spectrum of the mixture of conformers C and D supports the inverted orientation of the adjacent phenyl rings in the partial cone conformation (D).^{9,10}

2.1.1. Assignment of the resonances for the –CH₂– and –OCH₃ protons

All the –CH₂– and –OCH₃ protons for the A/B pair of conformers have been identified on the basis of the variation of shielding effect of the π -electron current of the aryl rings and through-space interaction among the proton signals of –CH₂– and –OCH₃ groups. To ascertain the latter, a phase sensitive ¹H–¹H NOESY experiment has been carried out at –30 °C, to suppress the exchange peaks and to obtain clear cross-peaks for through-space contacts (Fig. S2, see Supplementary data). Among the –CH₂– protons of the conformer (A), two equivalent H_a protons flanked by the π -electron cloud of two aryl rings would be expected to resonate at a relatively high field region. Hence the doublet at δ 3.10 is assigned to H_a protons. As

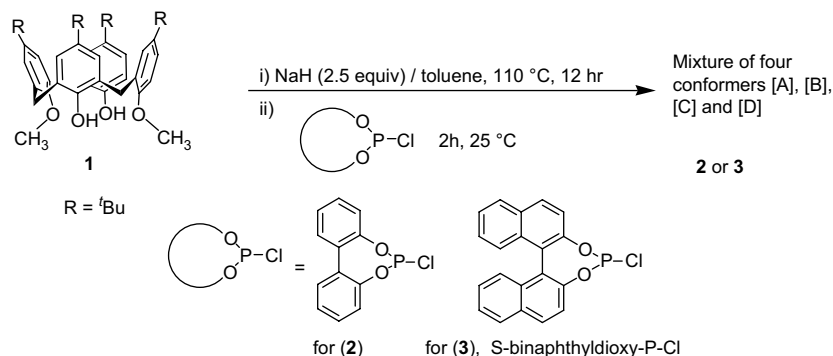
expected, the H_a signal shows a cross-peak with H_b, which resonates at relatively low field region at δ 4.69 due to the absence of any shielding effect of the aryl rings. Two additional NOE signals are observed between –OCH₃(2) and H_b, and between –OCH₃(2) and H_d protons. These cross-peaks together with another cross-peak between H_d and H_c establish the partial cone conformation of (A) and confirm the assignment of protons in the methylene region. Similarly the resonances of the protons of the conformer (B) have been assigned.

The resonances arising from the protons of the other pair of conformers (C/D) have been identified by following the same procedure as above except that instead of recording a low temperature NOESY spectrum, we have performed the ¹H–¹H COSY (Fig. S3, see Supplementary data) and room temperature NOESY (Fig. 1) experiments. The through-bond and through-space contacts are listed along with the corresponding spectra.

We have measured the rate constant *k* and ΔG^\ddagger for the exchange process between the conformers A and B as well as between C and D by monitoring the overlapping of the doublets at δ 4.91/4.73 and 4.71/4.48, respectively, at the coalescence temperature *T_c*, which is found to be +70 °C for both the pairs. The rate constant *k* and ΔG^\ddagger for the exchange process are calculated by using a standard method¹¹ and are 0.40 s^{–1}/87 kJ mol^{–1} and 0.51 s^{–1}/86 kJ mol^{–1}, respectively. The presence of sterically bulky biphenyldioxy units in the lower rim of the calixarene framework may be responsible for the higher magnitude of ΔG^\ddagger compared to the values previously reported.^{3d}

2.1.2. Mechanism for the exchange process

The assignment of the resonances arising from –CH₂– and –OCH₃ protons enabled us to study the mechanism of interconversion of A and B as well as that of C and D conformers. For both the pairs, NOESY spectra at room temperature have been recorded (see Fig. S4 in Supplementary data for A/B and Fig. 1 for C/D). Distinct cross-peaks with same phase with respect to the diagonal peaks signify the presence of exchange processes among the conformers. The exchange peaks for each of the two pairs have been analyzed and the predicted mechanism of interconversion of the conformers of the respective pairs are shown in Figures 2 and 3 along with the list of exchanging –CH₂– and –OCH₃ protons. Intense exchange peaks between H_a–H_b, H_a–H_e, H_b–H_g, H_b–H_f, H_c–H_f, H_d–H_e, OCH₃(1)–OCH₃(2) for the A/B pair of conformers indicates the flipping of one of the two aryl rings containing –OCH₃ as the *para*-substituent. This flipping would result in the conversion of partial cone (B or B') to 1,2-alternate (A or A') conformers. The intense cross-peaks between H_g–H_f, H_h–H_e and H_a–H_d, H_b–H_c point to the simultaneous rotation of both the –OCH₃ containing aryl rings, which would lead to the exchange of the two indistinguishable partial cone (B–B') topomers and also of the two indistinguishable



Scheme 1. Synthesis of ligands 2 and 3.

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