A calix[6]arene derived diphosphite, synthesis and complexation behaviour; X-ray structure of a palladium(II) chloride complex

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Calix[6]arene reacts with 2 equiv. of PCl_3 to form a bidentate diphosphite ligand L which coordinates to Pd, Pt and Re in a *cis* fashion and, according to X-ray analysis, with a bite angle of approximately 90° for a palladium complex $[PdCl_2L]$.

Numerous functional groups (phosphate, phosphine, phosphinite, amine, salen, porphyrin, crown ether, phosphite) have been attached to the calixarene backbone to make them suitable for transition-metal complexation.[1]

As an extension of our studies on bulky aryl(di)phosphites as ligands in transition-metal catalysts,[2] we are interested in calixarene phosphites which may provide bulky ligands with limited flexibility and well defined geometries. Diphosphites of larger calixarenes may enforce unusual bite angles. Previous studies have shown that these properties can have a large influence on the catalytic performance of rhodium-based hydroformylation catalysts.[3] Here we report on the synthesis of calix[6]arenediphosphite and some of its metal complexes.

Calix[6]arenediphosphite L was prepared from calix[6]arene and PCl_3. According to ^1H and ^{31}P NMR spectra a mixture of two components was obtained. The components were denoted *syn* and *anti* on the basis of ^1H NMR data and in analogy to a reported calix[6]diphosphate and 1,5-bridged calix[8]arene.[1a,4] The *syn* conformer was obtained in pure form by means of column chromatography and recrystallisation from hexane, thus yielding 20–40% of the new ligand. The assignment of the structure of the *anti* conformer was done on the basis of ^{31}P and ^1H NMR data in comparison with those for the *syn* conformer although the former could not be obtained in pure form.

Preliminary molecular modelling (MM2) with the CAChe system showed a natural bite angle for calix[6]arenediphosphite of almost 90° for a metal complex with the calixarene backbone attached to the phosphite groups in a so-called up–up–out or partial-cone conformation.[5] Previous studies on calixarene phosphates showed that this is a favourable conformation.[1a,g]

Complexes were made by mixing the ligand with a suitable metal precursor in dry CH_2Cl_2, thf or toluene, stirring for several hours and evaporating the solvent. The structures of the complexes, deduced from the NMR and IR data, are given below.

The ^{31}P NMR spectrum of $[PtCl_2L]$ **1** shows one signal with ^{195}Pt satellites with a very large J(Pt,P) (5800 Hz). We assume therefore that the ligand possesses a mirror plane situated between the two phosphorus atoms and bisecting the ligand (σ_1 in Fig. 1). ^1H NMR spectroscopy suggests a second mirror plane (σ_2 in Fig. 1), perpendicular to the first one and containing the two phosphorus atoms, because the Bu^t groups show two signals in a 1 : 2 ratio and the methylene bridges show two AB systems in a 1 : 2 ratio. This second mirror plane, however, could be a result of fluxional behaviour of the ligand, showing an average signal. NMR data do not exclude a *trans* complex, but modelling shows that a bite angle of 180° is highly unlikely.

The ^{31}P and ^1H NMR data of $[PdCl_2L]$ **2** are very similar to those of **1**. The ^{31}P NMR shows one singlet at δ 73.26 and the ^1H NMR data suggest two mutually perpendicular mirror planes in the ligand giving rise to two AB systems with relative intensity 1 : 2. Complex **2** afforded crystals suitable for X-ray analysis (see below).

The ^{31}P NMR spectra of [PtMe(Cl)L] **3** and [PdMe(Cl)L] **4** show two chemically inequivalent phosphorus atoms, coupled to one another with a typical *cis* coupling constant of 120 Hz. One of the signals is further split by the action of *trans* P–H coupling with the methyl group attached to the metal. In the case of **3** additional ^{195}Pt satellites are seen on both phosphorus signals with large coupling constants [J(Pt,P) = 7300 Hz, P *trans* to Cl; J(Pt,P) = 2700 Hz, P *trans* to Me]. These data clearly suggest a *cis* geometry of the ligand. The ^1H NMR data are in full agreement with these results, showing three AB systems in the methylene region with intensities 1 : 1 : 1 for both complexes corresponding with the equivalent methylene bridges a–a′, b–b′ and c–c′ in Fig. 1. Two-dimensional ^1H NMR of **4** clearly showed that the pseudo triplet at δ 3.50 consists of two doublets that are coupled with two other doublets at *ca.* δ 4.57. In the analogous spectrum of **3** we assume the same behaviour. Since **3** disproportionated into **1** and $[PtMe_2L]$, we have not been able to synthesize **3** in pure form. The assignment of the structure is based on ^{31}P and ^1H NMR data.

The $[Re(CO)_3Cl(L)]$ complex affords a special case in this series since the complex is octahedral. The ^{31}P NMR spectrum shows one signal, suggesting that the two phosphorus atoms are equivalent and therefore both must be *trans* to a CO molecule. This means the three CO molecules form one face of the octahedron, the chloride anion and the ligand forming the other face. This causes two inequivalent faces in the ligand with respect to the plane bisecting the ligand and containing both phosphorus atoms (see σ_2 in Fig. 1). The AB systems in the ^1H NMR spectrum are as expected. The facial arrangement of the CO molecules is confirmed by IR spectroscopy of the

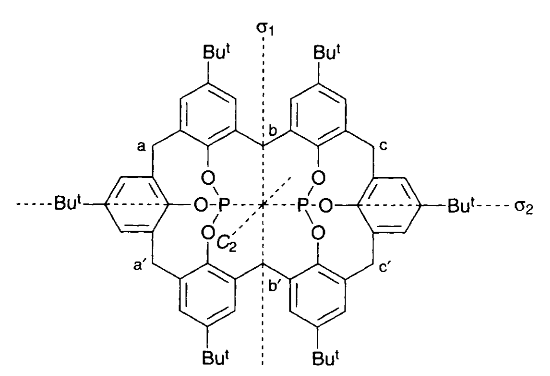

Fig. 1 Schematic drawing of the structure of L, showing symmetry relations

compound in KBr, which shows a typical set of signals which is clearly different from a meridional one.[6]

A drawing of the crystal structure of **2** is presented in Fig. 2† and clearly shows the conformation of the calixarene backbone in both phosphite moieties to be partial-cone (up–up–out).[1a,g] Bond lengths around the phosphorus atom are within the usual range for phosphites. Inspection of the angles around the Pd atom shows that the bite angle of the ligand is 94°. From these results we conclude that the actual structure is in good agreement with the molecular mechanics results. The ligand as a whole has only non-crystallographic C_2 symmetry, even in the complex, without a plane of symmetry, thus introducing chirality. However, as was mentioned before, the ^1H NMR results suggest a plane of symmetry in the complexes on the NMR timescale. We therefore conclude that in solution the ligand undergoes fluxional behaviour in the phosphite moieties (partial-cone/partial-cone interconversion). Until now, low-temperature NMR experiments (213 K) have not resulted in confirmation of this fluxional behaviour.

In summary, the calix[6]arene affords a fairly rigid backbone to which phosphite groups have been easily attached. A bidentate ligand results with limited flexibility and a well defined bite angle that enforces the ligand to coordinate in a purely *cis* fashion. Molecular mechanics have provided a fairly accurate prediction of the ligand properties of calix[6]arene-diphosphite.

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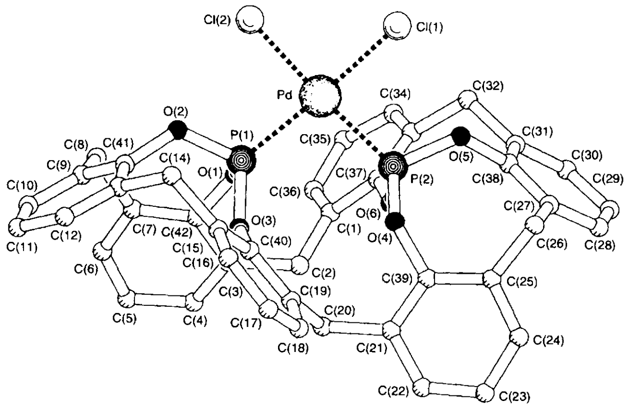

Fig. 2 Crystal structure of **2**. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.237(2), Pd–P(2) 2.236(2), Pd–Cl(1) 2.309(3), Pd–Cl(2) 2.317(2), P(1)–O(1) 1.571(6), P(1)–O(2) 1.578(5), P(1)–O(3) 1.582(5), P(2)–O(4) 1.581(5), P(2)–O(5) 1.583(6), P(2)–O(6) 1.580(6); Cl(1)–Pd–Cl(2) 86.73(9), P(1)–Pd–P(2) 94.09(7), Cl(1)–Pd–P(2) 89.66(8), Cl(2)–Pd–P(1) 89.51(8).

Footnote

† *Crystal data* for compound **2**, $C_{66}H_{78}Cl_2O_6P_2Pd$, M_r = 1206.61, yellow, block-shaped crystal (0.2 × 0.2 × 0.2 mm), orthorhombic, space group $P2_12_12_1$ with a = 17.5161(15), b = 19.6126(13), c = 21.838(3) Å, U = 7502.1(13) Å^3, Z = 4, D_c = 1.068(2) g cm^{-3}, $F(000)$ = 2528, μ(Mo-Kα) = 4.0 cm^{-1}. All data, where relevant, are given without disordered solvent contribution (see below). 9721 Reflections measured, 9656 independent, ($0.93 < \theta < 27.49°$, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.710 73 Å) on an Enraf-Nonius CAD4-T diffractometer. Data were not corrected for absorption. The structure was solved by automated Patterson methods (SHELXS86). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criteron was applied during refinement. Connected channels, with a total volume of 2203 Å^3 per unit cell, were found to be filled with disordered solvent molecules. No satisfactory model could be refined. This disordered density (461 electrons per unit cell) was taken into account with the BYPASS procedure, as implemented in PLATON. The Flack x parameter refined to 0.22(5). Refinement converged at a $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5} = 0.125$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.063$ [for 5134 reflections with $I > 2\sigma(I)$], S = 0.84, for 713 parameters. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. A final difference Fourier map showed no residual density outside −0.64 and 0.80 e Å^{-3} (near Pd). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 (*a*) F. Grynszpan, O. Aleksiuk and S. E. Biali, *J. Chem. Soc., Chem. Commun.*, 1993, 13; (*b*) W. Xu, J. P. Rourke, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, 1995, **34**, 323; (*c*) D. M. Rudkevich, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1994, **59**, 3683; (*d*) O. Aleksiuk, F. Grynszpan and S. E. Biali, *J. Org. Chem.*, 1993, **58**, 1994; (*e*) Z. Asfari, J. Vicens and J. Weiss, *Tetrahedron Lett.*, 1993, **34**, 627; (*f*) Y. Okada, F. Ishii, Y. Kasai and J. Nishimura, *Tetrahedron Lett.*, 1993, **34**, 1971; (*g*) D. V. Khasnis, J. M. Burton, M. Lattman and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1991, 562; (*h*) C. Dieleman, C. Loeber, D. Matt, A. De Cian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1995, 3097; (*i*) B. R. Cameron, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Org. Chem.*, 1995, **60**, 2802; (*j*) C. Loeber, C. Wieser, D. Matt, A. De Cian, J. Fischer and L. Toupet, *Bull. Soc. Chim. Fr.*, 1995, **132**, 166.

2 G. J. H. Buisman, E. J. Vos, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, 1995, 409; A. van Rooy, E. N. Orij, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Organometallics*, 1995, **14**, 34.

3 C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney and D. R. Powell, *J. Am. Chem. Soc.*, 1992, **114**, 5535; C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

4 F. Cunsolo, M. Piatelli and P. Neri, *J. Chem. Soc., Chem. Commun.*, 1994, 1917.

5 CAChe Worksystem, version 3.7, Portland OR, 1994.

6 G. J. Stor, F. Hartl, J. W. M. van Outersterp and D. J. Stufkens, *Organometallics*, 1995, **14**, 115.

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