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Multifunctional phosphane and phosphane oxide ligands derived from *p*-tert-butylcalix[4]arene. Synthesis of a large diphosphane with C_2 symmetry and behaving as a *cis* or *trans* binding ligand

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Abstract

The calix[4]arene derived di(phosphane oxide) **2** (cone conformation) was obtained in 78% yield by treatment of **1** with 2 equiv NaO^tBu followed by reaction with 2 equiv $Ph_2P(O)CH_2OTs$. When KO^tBu was used instead of NaO^tBu, the partial cone isomer **2′** was formed. Reaction of **2** with $PhSiH_3$ in refluxing toluene afforded quantitatively the mixed di(ester)-di(phosphane) ligand **3**; crystal data of **3**: monoclinic, $C2/c$; $a = 24.091(7)$, $b = 14.416(4)$, $c = 25.270(8)$ Å, $\beta = 128.07(2)°$, $V = 6909.1(5)$ Å^3, $Z = 4$ and $R_F = 5.8\%$. The molecule which lies on a C_2 axis adopts a distorted cone conformation; the angle formed between the ester substituted phenolic rings is 10.5(2)° and that between the phosphane substituted rings is 95.0(1)°. The phosphorus lone pairs point towards the exterior of the space defined by the four calixarene substituents, whereas the two ester groups are directed to the interior of this cavity. Ligand **3** reacts with $[PtCl_2(PhCN)_2]$ in THF to yield *cis*-$PtCl_2 \cdot$ **3** (**4**) in 91% yield. The sequential reaction of $[RhCl(1,5\text{-cyclooctadiene})]_2$ with 2 equiv $AgBF_4$ and 2 equiv **3** gave the cationic complex *cis*-[Rh(1,5-cyclooctadiene) · **3**](BF_4) (**5**). Reaction of carbon monoxide with commercial $RuCl_3$ in boiling 2-ethoxyethanol and subsequent addition of **3** gave *cis-cis-trans-P,P*-[$RuCl_2(CO)_2 \cdot$ **3**] (**6**). Complexes **4–6** display fluxional behaviour in solution. All compounds were characterized by elemental analysis and IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

Key words: Phosphane; Platinum; Rhodium; Ruthenium; Calixarene; Macrocycle

1. Introduction

Multifunctional phosphane ligands are of increasing interest [1], in particular for the study of reactive, coordinatively unsaturated transition metal complexes [2]. As a part of a programme [3] to develop hybrid diphosphane ligands of catalytic relevance, we set out to prepare ligands derived from *p*-tert-butylcalix[4]arene. Calix[4]arenes may easily be functionalized at the hydroxyl groups (lower rim) and therefore are valuable preorganizing matrices for the construction of tetradentate ligands [4]. Despite their attractive architecture, only very few ligands derived from such a macrocyclic subunit have been used for the complexation of transition metal ions [5,6]; most of the metallocalixarenes reported to date have the metal bonded directly to the phenolic oxygen centres [7]. Tetrafunctional calixarenes in the so-called cone conformation with adequate binding functions, *e.g.* phosphanes, connected to the lower rim may be suitable for transition metal encapsulation or could lead to transition metal complexes combining the properties of cavity shaped molecules with those of metal centres. This latter point could be particularly relevant for site selectivity in catalytic reactions [8]. Furthermore, with butylcalix[4]arene derivatized ligands in which the four lower rim substituents are a combination of phosphane moieties

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and weak donor atoms, the synthesis of monoligand complexes allowing the spontaneous generation of vacant sites may in principle be achieved. Such tetradentate hybrid ligands are also likely to favour anchimeric assistance in transition metal-catalyzed reactions and present a rare opportunity to study the effects of a mixed-ligand environment on the properties of a metal centre. We report the first example of a chelating diphosphane ligand and the corresponding bis-(phosphane oxide) built on the lower rim of a calix[4]arene matrix.

2. Experimental details

2.1. General

All reactions were performed under argon using Schlenk tube techniques. The work-up of the phosphane oxides **2** and **2'** does not require manipulation under argon. Solvents including $CDCl_3$ were purified and dried by conventional methods and stored under argon. IR spectra were recorded on a IFS 25 Bruker spectrometer. All NMR measurements were performed on a FT-Bruker WP 200 SY spectrometer. The ^{1}H NMR data were referenced relative to residual protiated solvents (7.26 ppm for $CDCl_3$); the ^{13}C NMR chemicals shifts are reported relative to $CDCl_3$ (77.0 ppm) and the ^{31}P NMR data are given relative to external 85% H_3PO_4. For the variable temperature NMR studies, sealed tubes were used. The mass spectra were recorded on a TSQ70 Finnigan MAT (for compounds **2**, **2'** and **3**) or on a ZAB HF VG Analytical using *m*-nitrobenzylalcohol as matrix for complexes **4** and **6** and tetraglyme for **5**. The compounds $Ph_2P(O)CH_2OTs$ [9], 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (cone) (**1**) [10], $PtCl_2(PhCN)_2$ [11] and [RhCl(1,5-cyclooctadiene)]$_2$ [12] were prepared according to literature procedures. Ruthenium trichloride was from Johnson Matthey and phenylsilane from Aldrich.

2.2. Preparation of 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (cone) (2)

A solution of 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (cone) (**1**) (30.300 g, 36.90 mmol) in a THF-DMF (9:1, v/v) mixture (1000 ml) was refluxed with ^{t}BuONa (8.735 g, 90.89 mmol) for 1 h. Then $Ph_2P(O)CH_2OTs$ (31.370 g, 81.18 mmol) was added and the solution refluxed for 60 h. After filtration, the solvents were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (500 ml) and the resulting solution washed with water (2 × 300 ml). During this step the aqueous solution was maintained at pH 7 using 1 N HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated to *ca*. 50 ml. Addition of acetone under stirring and cooling gave **2** as a white powder ($R_F = 0.41$ in CH_2Cl_2/MeOH, 94:6, v/v) (yield 36.005 g, 78%). m.p. 234–239°C. IR (KBr): $\nu = 1753$s (C=O) cm^{-1}; ν(P=O) not assigned due to bands of the calixarene part near 1190 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.84–7.74 and 7.51–7.34 (m, 20H, PPh_2), 6.77 (s, 4H, *m*-ArH), 6.42 (s, 4H, *m*-ArH), 5.20 (s, 4H, OCH_2PPh_2), 4.63 (s, 4H, OCH_2CO_2Et), 4.69 and 2.96 (AB spin system, 8H, $ArCH_2Ar$, $J(AB) = 13.1$ Hz), 4.11 (q, 4H, CH_2CH_3, $^3J = 7.1$ Hz), 1.23 (t, 6H, CH_2CH_3, $^3J = 7.1$ Hz), 1.11 (s, 18H, ^{t}Bu), 0.93 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 170.86 (s, C=O), 153.04–132.58 (aromatic C_{quat}), 131.35, 131.17, 128.38, 128.15, 125.40 and 124.79 (aromatic CH), 71.82 (d, $OCH_2P(O)Ph_2$, $J(PC) = 78.6$ Hz), 70.94 (s, OCH_2CO_2Et), 60.12 (s, OCH_2CH_3), 33.73 and 33.60 (2s, $C(CH_3)_3$), 32.03 (s, $ArCH_2Ar$), 31.32 and 31.22 (2s, $C(CH_3)_3$), 14.19 (s, OCH_2CH_3). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 24.93 (s, Ph_2P=O). MS (CI), *m/z*(%): 1249 (69) $[M + H^+]$. Anal. Found: C, 75.00; H, 7.51. $C_{78}H_{90}O_{10}P_2$ (1249.53) calcd: C, 74.98; H, 7.26%.

2.3. Preparation of 26,28-anti-5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis (diphenylphosphinoylmethoxy)calix[4]arene (partial cone) (2')

A solution of 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (cone) (4.543 g, 5.53 mmol) in a THF-DMF (9:1 v/v) mixture (250 ml) was refluxed with ^{t}BuOK (1.400, 12.48 mmol) for 1 h. Then $Ph_2P(O)CH_2OTs$ (4.487 g, 11.61 mmol) was added and the solution refluxed for 60 h. After filtration, the solvents were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (150 ml) and washed with water (2 × 100 ml) (the aqueous solution was maintained at pH 7). After filtration, the organic layer was dried over $MgSO_4$, filtered and concentrated to *ca*. 10 ml. Addition of acetone under stirring and cooling gave compound **2'** as a white powder ($R_F = 0.33$; CH_2Cl_2/MeOH 94:6, v/v) (yield 5.2 g, 75%). m.p. 285–290°C. IR (KBr): $\nu = 1755$s cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.77–7.65 and 7.45–7.27 (m, 20H, PPh_2), 7.23 (s, 2H, *m*-ArH), 6.99 and 6.34 (AB spin system, 4H, *m*-ArH, $^4J(AB) = 2$ Hz), 6.60 (s, 2H, *m*-ArH), 4.95 (s, 2H, $OCH_2P(O)Ph_2$), 4.70 (s, 2H, $OCH_2P(O)Ph_2$), 4.68 and 4.50 (AB spin system, 4H, OCH_2CO_2Et, $J(AB) = 16$ Hz), 4.57 and 2.84 (AB spin system, 4H, $ArCH_2Ar$, $J(AB) = 13.4$ Hz), 4.22 (m, ABX_3 spin system, 4H, CH_2CH_3), 3.80 (broad s, 4H, $ArCH_2Ar$), 1.31 (t, 6H, CH_2CH_3, $^3J = 7.1$ Hz), 1.22 (s, 9H, ^{t}Bu), 1.12 (s, 9H, ^{t}Bu), 0.92 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 170.16 (s, C=O), 155.35–130.36 (aromatic C_{quat}), 131.82, 131.78, 131.14, 130.95, 130.92, 130.73, 130.59, 128.67, 128.44, 128.28, 127.89, 127.66, 125.60 and 124.90 (aromatic CH), 71.25 (s, OCH_2CO_2Et), 70.77 (d, $OCH_2P(O)Ph_2$, $J(PC) = 80.4$ Hz), 68.45 (d, $OCH_2P(O)Ph_2$, $J(PC) = 70.0$ Hz), 60.52 (s, OCH_2CH_3), 36.46 (s, *anti*-$ArCH_2Ar$), 33.81 and 33.61 (2s, $C(CH_3)_3$), 32.21 (s, *syn*-$ArCH_2Ar$), 31.52, 31.39 and 31.28 (3s, $C(CH_3)_3$), 14.27 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 24.37 and 21.82 (2s, $Ph_2P{=}O$). MS (CI), *m/z* (%): 1249(17) [$M + H^+$]. Anal. Found: C, 75.09; H, 7.46. $C_{78}H_{90}O_{10}P_2$ (1249.53) calcd: C, 74.98; H, 7.26%.

2.4. Preparation of 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinomethoxy)calix[4]arene (cone) (3)

A mixture of the bis(phosphane oxide) **2** (5.00 g, 4.00 mmol) and phenylsilane (8.657 g, *ca.* 10 ml, 80.0 mmol) in toluene (60 ml) was refluxed for 2 days. The solvent was removed *in vacuo* and the residue was chromatographed over silica gel 60 (25 g, 70-230 mesh) using CH_2Cl_2 (70 ml) as eluant ($R_F = 0.95$, CH_2Cl_2) (yield 4.67 g, 96%). m.p. 220–225°C. IR (KBr): $\nu = 1758$s cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.52–7.42 and 7.33–7.28 (m, 20H, PPh_2), 6.89 (s, 4H, *m*-ArH), 6.51 (s, 4H, *m*-ArH), 4.97 (d, 4H, OCH_2PPh_2, $J(PH) = 3.1$ Hz), 4.61 (s, 4H, OCH_2CO_2Et), 4.60 and 3.07 (AB spin system, 8H, $ArCH_2Ar$, $J(AB) = 13$ Hz). 4.16 (q, 4H, CH_2CH_3, $^3J = 7.1$ Hz), 1.27 (t, 6H, CH_2CH_3, $^3J = 7.1$ Hz, 1.19 (s, 18H, ^tBu), 0.94 (s, 18H, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.62 (s, C=O), 153.70–132.57 (aromatic C_{quat}), 133.33, 132.98, 128.53, 128.41, 128.27, 125.53 and 124.75 (aromatic CH), 76.95 (d, OCH_2PPh_2, $J(PC) = 8.6$ Hz), 70.75 (s, OCH_2CO_2Et), 60.25 (s, OCH_2CH_3), 33.88 and 33.69 (2s, $C(CH_3)_3$), 32.23 (s, $ArCH_2Ar$), 31.50 and 31.26 (2s, $C(CH_3)_3$), 14.30 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): $\delta - 22.1$ (s, PPh_2). MS (CI), *m/z* (%): 1217 (14) [$M + H^+$]. Anal. Found: C, 76.89; H, 7.57. $C_{78}H_{90}O_8P_2$ (1217.53) calcd.: C, 76.95 H, 7.45%.

2.5. Preparation of cis-dichloro, 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinomethoxy)calix[4]arene platinum (II) (4)

To a solution of $PtCl_2(PhCN)_2$ (0.132 g, 0.28 mmol) in THF (30 ml) was added dropwise a solution of **3** (0.354 g, 0.29 mmol) in THF (20 ml). After 1 h the solution was concentrated to 5 ml and diethyl ether was added to yield **4** as an analytically pure white powder (yield 0.378 g, 91%). m.p. 275–280°C. IR (KBr): $\nu = 1757$s and 1732s cm^{-1} (C=O). ^1H NMR ($CDCl_3$, 378 K): δ 7.58–7.10 (20H, PPh_2), 6.86 (s, 4H, *m*-ArH), 6.12 (s, 4H, *m*-ArH), 5.37 (broad signal, 4H, OCH_2PPh_2), 4.17 (s, 4H, OCH_2CO_2Et), 4.07 (q, 4H, CH_2CH_3, $^3J = 7.0$ Hz), 3.91 and 2.65 (AB spin system, 8H, $ArCH_2Ar$, $J(AB) = 13$ Hz), 1.30 (s, 18H, ^tBu), 1.18 (t, 6H, CH_2CH_3, $^3J = 7.1$ Hz), 0.78 (s, 18H, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 345 K): δ 169.70 (s, C=O), 154.62–124.43 (aromatic C's), 73.45 (m, OCH_2PPh_2), 70.23 (s, OCH_2CO_2Et), 60.29 (s, OCH_2CH_3), 33.76 and 33.29 (2s, $C(CH_3)_3$), 31.88 (s, $ArCH_2Ar$), 31.40 and 30.91 (2s, $C(CH_3)_3$), 14.03 (s, OCH_2CH_3). $^{31}P\{^1H\}$NMR (CH_2Cl_2/C_6D_6): δ 7.7 (broad s with Pt satellites, PPh_2, $J(PPt) = 3536$ Hz). MS (FAB), *m/z* (%): 1447 (8) [$(M - Cl)^+$], 1411(24) [$(M - Cl - HCl)^+$]. Anal. Found: C, 63.18; H, 6.09. $C_{78}H_{90}Cl_2O_8P_2Pt$ (1483.53) calcd.: C, 63.15 H, 6.11%.

2.6. Preparation of cis-P,P-5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinomethoxy)calix[4]arene-1,5-(cyclooctadiene) rhodium (I) tetrafluoroborate (5)

To a a solution of [RhCl(1,5-cyclooctadiene)]$_2$ (0.050 g, 0.10 mmol) in CH_2Cl_2 (2 ml) was added dropwise a solution of $AgBF_4$ (0.040 g, 0.21 mmol) in THF (1 ml). The solution was carefully filtered over celite and directly added to a solution of **3** (0.255 g, 0.21 mmol) in CH_2Cl_2 (15 ml). After 2 h the solution was concentrated to *ca.* 2 ml and Et_2O was added to afford **5** as a yellow powder (yield 0.130 g, 86%). m.p. 220°C (dec). IR (nujol): $\nu = 1743$s and 1715s cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 8.17–8.03 and 7.76–7.32 (m, 20H, PPh_2), 6.94 (s, 4H, *m*-ArH), 6.42 (s, 4H, *m*-ArH), 5.64 (broad signal 4H, OCH_2PPh_2), 4.32 (broad signal, 4H, HC=CH of COD), 4.31 (q, 4H, CH_2CH_3, $^3J = 7.1$ Hz), 4.06 and 2.92 (AB spin system, 8H, $ArCH_2Ar$, $J(AB) = 13.5$ Hz), 3.77 (s, 4H, OCH_2CO_2Et), 2.38 (m, 4H, CH_2 of COD), 2.13 (m, 4H, CH_2 of COD), 1.37 (t, 6H, CH_2CH_3, $^3J = 7.2$ Hz), 1.28 (s, 18H, ^tBu), 0.76 (s, 18H, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 170.47 and 169.34 (2s, C=O), 154.70–125.01 (aromatic C's), 100.12 and 98.31 (2s broad, CH=CH of COD), 72.70–70.27 (m, unresolved signals due to OCH_2PPh_2 and OCH_2CO_2Et), 61.08 and 60.56 (2s, OCH_2CH_3), 33.85, 33.65 and 33.42 (3s, $C(CH_3)_3$), 31.51 and 30.97 ($C(CH_3)_3$), 30.30 and 29.99 (2s, CH_2 of COD), 14.28 and 14.13 (2s, OCH_2CH_3); the $ArCH_2$ signals are masked by those of $C(CH_3)_3$. $^{31}P\{^1H\}$NMR (CH_2Cl_2/C_6D_6): δ 18.8 (d, PPh_2, $^2J(PRh) = 141.0$ Hz). MS (FAB), *m/z* (%): 1443(40) [$(M - BF_4 + O)^+$], 1427(11) [$(M - BF_4)^+$]. Anal. Found: C, 67.28; H, 6.72. $C_{86}H_{102}BF_4O_8P_2Rh \cdot 0.25\ CH_2Cl_2$(1515.43 + 21.23) calcd.: C, 67.35 H, 6.74%.

2.7. Preparation of cis-dichloro, cis-dicarbonyl, trans-P,P-5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinomethoxy)calix[4]arene ruthenium (II) (6)

Carbon monoxide was bubbled through a boiling solution of commercial ruthenium trichloride (0.080 g, *ca.* 0.33 mmol) in 2-ethoxyethanol. After 20 min solid **3** (0.406 g, 0.33 mmol) was added to the hot solution. The solution was allowed to cool to room temperature, while maintaining the CO bubbling for *ca.* 20 min. The solvent was evaporated to dryness and the residue recrystallized in CH_2Cl_2/pentane affording **6** as a white microcrystalline powder (yield 0.401 g, 84%). m.p. > 270°C. IR (KBr) (cm^{-1}): ν (C ≡ O) 2053s, 1990s; ν (C=O) 1758s and 1733s. IR (nujol): ν = 2052s, 1988s (C ≡ O); ν = 1748s and 1719s cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.88–7.36 (m, 20H, PPh_2), 6.85 (s, 4H, *m*-ArH), 5.98 (s, 4H, *m*-ArH), 5.89 (broad signal 4H, OCH_2PPh_2), 4.27 (s broad, 4H, OCH_2CO_2Et), 4.20 (q, 4H, CH_2CH_3, $^3J = 7.2$ Hz), 4.07 and 2.73 (4 broad signals, AB spin system, 8H, $ArCH_2Ar$, $J(AB) = 13$ Hz), 1.25 (s, 18H, ^tBu), 1.20 (t, 6H, CH_2CH_3, $^3J = 7.2$ Hz), 0.70 (s, 18H, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 330 K): δ 192.39 (t, C≡O, $^2J(PC) = 9.5$ Hz), 170.03 (s, C=O), 154.71, 153.27, 144.75, 143.51, 134.63, 128.62 and 127.72 (aromatic C_{quat}), 133.17, 130.38, 128.11, 125.97 and 124.29 (aromatic CH), 71.09 (broad signal, OCH_2PPh_2), 70.34 (s, OCH_2CO_2Et), 60.47 (s, OCH_2CH_3), 33.76 and 33.24 (2s, $C(CH_3)_3$), 32.09 (s, $ArCH_2Ar$), 31.44 and 30.94 (2s, $C(CH_3)_3$), 14.17 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 18.8 (s, PPh_2). MS (FAB), *m/z* (%): 1381(7) [M − Cl − CO + H^+]. Anal. Found: C, 63.83; H, 6.40. $C_{80}H_{90}Cl_2O_{10}P_2Ru \cdot CH_2Cl_2$ (1445.53 + 84.93) calcd.: C, 63.57 H, 6.06%.

2.8. *X-ray data collection and refinement*

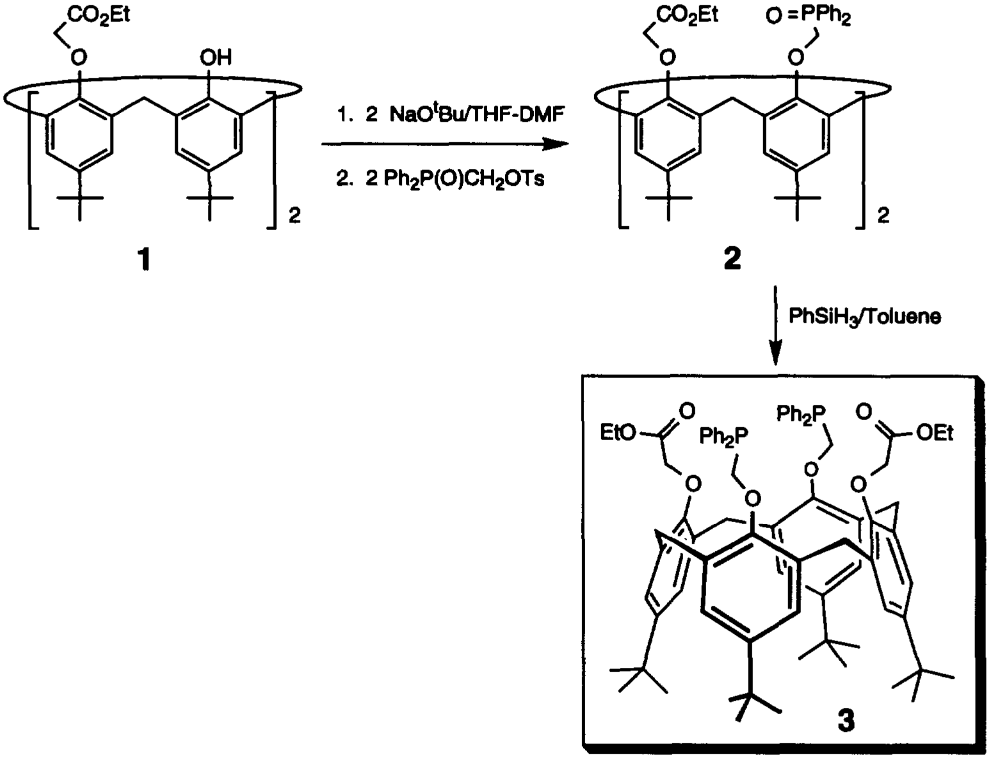
A summary of the crystallographic data for **3** is given in Table 1. Colourless crystals suitable for diffraction were obtained by slow diffusion of ethanol into a toluene solution of the compound. The unit cell was obtained from the angular settings of 25 reflections (19° ≤ θ ≤ 21°); 3925 reflections were collected on a Philips PW 1100/16 diffractometer (6° ≤ 2θ ≤ 102°); 2538 with $I > 3\sigma(I)$ were used for determination and refinement of the structure. No decay was observed during the data collection period. For all subsequent computations the Enraf-Nonius MOLEN package was used [13]. Intensities were corrected for Lorentz, polarization and absorption factors, the latter using the gaussian method. The structure was solved using MULTAN and refined by full matrix least-squares with anisotropic thermal parameters for all non hydrogen atoms. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 4I/\sigma^2(I) + (0.08I)^2$. Hydrogen atoms were introduced at their computed coordinates (C–H = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of $B = 1.3\ B_{equiv}(C)$ Å^2. The final difference map showed no significant residual peaks. The neutral-atom scattering factors used for all atoms and anomalous scattering factors for all non hydrogen atoms were obtained from standard sources [14]. Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table 2. The following tables are available from the Cambridge Crystallographic Data Centre or from J.F.: hydrogen atom positional parameters (Table S1), a complete set of bond distances (Table S2), a complete set of bond angles (Table S3), observed structure factors and amplitudes for all observed reflections (Table S4).

TABLE 1. Structure determination summary for **3**

formula	$C_{78}H_{90}O_8P_2$
Formula weight	1217.5
Crystal system	monoclinic
Space group	$C2/c$ (No. 15)
a(Å)	24.091(7)
b(Å)	14.416(4)
c(Å)	25.270(8)
β(°)	128.07(2)
V(Å^3)	6909.1(5)
Z	4
D_{calc}(g cm^{-3})	1.170
T	173 K
F(000)	2608
μ (cm^{-1})	9.793
Min., max. transmission coefficients	0.78, 1.21
Range of collected data (°)	$3 < \theta < 51$
Scan type	$\omega - 2\theta$
No. of unique reflections	3925
$n(I) < n\sigma(I)$	3
No. of parameters refined	2538
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert \lvert \Sigma F_o \rvert$	0.058
$R_\omega = [\Sigma w(\lVert F_o \rvert - \lvert F_c \rVert)^2 / \Sigma w(\lvert F_o \rvert)^2]^{1/2}$	0.079
Weighting scheme	$\omega = 4I/\sigma^2(I) + (0.08I)^2$
Largest final shift/esd	0.03

3. Results and discussion

The construction of the calixarene-phosphane **3** was achieved starting from 5,11,17,23-tetra-tert-butyl-25,-27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (**1**) (cone conformation) [10] (Scheme 1). Treatment of this diester with 2.5 equiv NaO^tBu in a refluxing THF-DMF mixture and subsequent reaction with $Ph_2P(O)CH_2OTs$ (Ts = p-$MeC_6H_5SO_2$) gave the diester-di(phosphane oxide) **2** in 78% yield. As may unambiguously be deduced from the large [15] chemical shift difference (1.73 ppm) between the non equivalent $ArCH_2Ar$ protons, compound **2** has a cone conformation. This geometry is also confirmed by the chemical shift value of the corresponding carbon atoms (δ 32.03 ppm) which lie in the expected range for carbon atoms bridging two neighbouring phenolic rings in a *syn* arrangement [16]. When the reaction was



Scheme 1.

performed with KO^{t}Bu instead of NaO^{t}Bu, compound 2′ which has a partial cone conformation was selectively formed in 80% yield. The observed difference in reactivity when using KO^{t}Bu may be assigned to a weaker potassium *vs.* sodium binding in the corresponding diphenolates, a situation which is likely to favour a rocking of one of the ArO$^-$ moieties and thus lead to a partial cone conformer. For calixarenes, dependence on the conformation of the base used for functionalization of the phenolic parts has already been stressed [3,17].

Treatment of 2 with excess $PhSiH_3$ in refluxing toluene yielded the diphosphane 3. It is noteworthy that the ester groups are not reduced during this reaction, allowing the selective formation of 3. The ^{31}P NMR spectrum of 3 displays a singlet at −22.1 ppm. The ^1H and ^{13}C NMR data are consistent with a cone conformation (see Experimental part). The solid state structure of 3 has been elucidated by a single crystal X-ray crystallographic study. The ORTEP [18] structure of 3 is represented in Fig. 1 together with the numbering scheme. The molecule is located on a crystallographic two-fold axis. The shape of the calixarene deviates from an ideal cone conformation and may be viewed as a pinched cone: the dihedral angle between the aryl rings bearing the ester chains is 10.5(2)°, whereas that between the aryl rings substituted by the phosphane moieties is 95.0(1)°. The two CO_2Et groups are pointing toward the interior of the pocket formed by the four phenolate substituents and the phosphane chains are folded away from this cavity. The phosphorus atoms have the expected pyramidal geometry. It should be noted that the phosphorus lone pairs are directed towards the exterior of the substituent pocket. The three P–C bond lengths lie in the usual range for P–C single bonds (see Table 2). The P-P′ distance is 7.2(1) Å.

Ligand 3 reacts with $PtCl_2(PhCN)_2$ in THF to afford in *ca.* 95% spectroscopic yield complex 4 which was characterized by FAB MS and IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy (eqn. (1)). Complex 4 is highly soluble in CH_2Cl_2, THF and toluene.

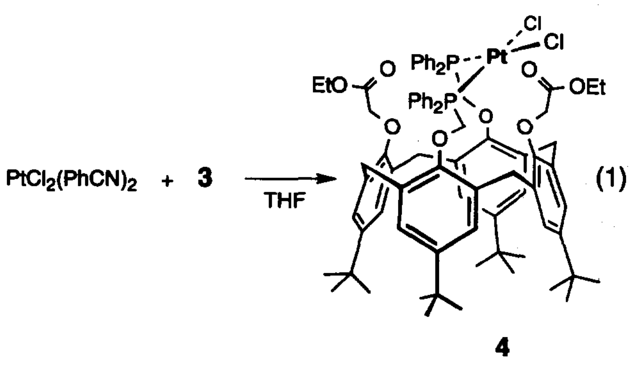


TABLE 2. Atomic coordinates and equivalent isotropic thermal factors for **3**

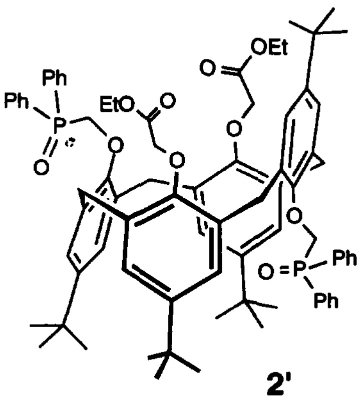
	x	*y*	*z*	*B* (Å^2) [a]
C(1)	0.4271(2)	0.1812(3)	0.6161(2)	3.6(1)
C(2)	0.4713(2)	0.1477(3)	0.6028(2)	3.5(1)
C(3)	0.4447(2)	0.0832(3)	0.5519(2)	4.0(1)
C(4)	0.3762(2)	0.0499(3)	0.5143(2)	4.0(1)
C(5)	0.3335(2)	0.0843(4)	0.5302(2)	4.1(1)
C(6)	0.3584(2)	0.1487(3)	0.5810(2)	3.6(1)
O(1)	0.4530(1)	0.2414(2)	0.6686(1)	3.82(7)
C(7)	0.4496(2)	0.3391(3)	0.6571(2)	4.2(1)
P	0.38525(6)	0.3772(1)	0.56865(5)	4.46(3)
C(8)	0.3919(2)	0.5026(4)	0.5805(2)	4.6(1)
C(9)	0.4375(3)	0.5492(4)	0.6403(2)	6.9(2)
C(10)	0.4369(3)	0.6447(4)	0.6435(3)	8.8(2)
C(11)	0.3906(3)	0.6948(4)	0.5872(2)	8.4(2)
C(12)	0.3459(3)	0.6512(4)	0.5274(3)	7.6(2)
C(13)	0.3464(3)	0.5559(4)	0.5242(2)	6.2(2)
C(14)	0.4353(2)	0.3635(4)	0.5361(2)	4.9(1)
C(15)	0.4984(2)	0.4076(4)	0.5630(2)	6.5(2)
C(16)	0.5338(3)	0.3932(5)	0.5372(3)	8.5(2)
C(17)	0.5068(3)	0.3338(5)	0.4850(3)	10.5(2)
C(18)	0.4446(3)	0.2893(5)	0.4566(2)	9.4(2)
C(19)	0.4080(3)	0.3036(4)	0.4826(2)	7.2(2)
C(20)	0.3496(2)	−0.0219(4)	0.4585(2)	5.1(1)
C(21)	0.3996(3)	−0.1053(4)	0.4873(3)	7.6(2)
C(22)	0.3512(3)	0.0213(5)	0.4045(2)	6.4(2)
C(23)	0.2762(3)	−0.0557(6)	0.4273(3)	9.5(2)
C(24)	0.3145(2)	0.1794(3)	0.6020(2)	3.8(1)
C(25)	0.3412(2)	0.1315(3)	0.6676(2)	3.4(1)
C(26)	0.3751(2)	0.1785(3)	0.7282(2)	3.3(1)
C(27)	0.4076(2)	0.1315(3)	0.7885(2)	3.4(1)
C(28)	0.4008(2)	0.0357(3)	0.7862(2)	3.8(1)
C(29)	0.3641(2)	−0.0149(3)	0.7267(2)	3.8(1)
C(30)	0.3356(2)	0.0356(3)	0.6684(2)	3.9(1)
O(2)	0.3805(1)	0.2750(2)	0.7290(1)	3.77(7)
C(31)	0.3320(2)	0.3219(4)	0.7331(2)	4.6(1)
C(32)	0.3509(2)	0.4232(4)	0.7446(2)	4.6(1)
O(3)	0.3896(2)	0.4605(3)	0.7371(2)	6.6(1)
O(4)	0.3199(1)	0.4656(3)	0.7660(1)	5.91(9)
C(33)	0.3331(3)	0.5654(4)	0.7786(3)	6.8(2)
C(34)	0.2908(3)	0.6008(5)	0.7970(3)	9.5(2)
C(35)	0.3568(2)	−0.1189(3)	0.7255(2)	4.8(1)
C(36)	0.3755(5)	−0.1624(6)	0.6894(4)	23.3(3)
C(37)	0.3896(7)	−0.1605(6)	0.7898(4)	20.5(6)
C(38)	0.2812(5)	−0.1433(6)	0.6874(7)	21.0(7)
C(39)	0.5470(2)	0.1795(3)	0.6441(2)	3.8(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{1,1}+b^2B_{2,2}+c^2B_{3,3}+ab(\cos\gamma)B_{1,2}+ac(\cos\beta)B_{1,3}+bc(\cos\alpha)B_{2,3}]$

TABLE 3. Bond lengths (Å) and angles (deg) for **3**)

P–C(7)	1.851(5)	C(26)–O(2)	1.397(5)
P–C(8)	1.824(6)	O(2)–C(31)	1.408(6)
P–C(14)	1.843(6)	C(31)–C(32)	1.504(8)
C(7)–O(1)	1.431(6)	C(32)–O(3)	1.189(6)
O(1)–C(1)	1.373(5)	C(32)–O(4)	1.314(6)
C(2)–C(39)	1.510(7)	O(4)–C(33)	1.465(7)
C(6)–C(24)	1.513(7)	C(33)–C(34)	1.450(9)
C(24)–C(25)	1.523(7)		
C(4)–C(20)	1.536(7)		
C(29)–C(35)	1.508(7)		
C(8)–P–C(14)	99.5(2)	C(6)–C(24)–C(25)	109.4(4)
C(14)–P–C(7)	102.5(2)	C(26)–O(2)–C(31)	113.8(3)
C(8)–P–C(7)	99.9(3)	O(2)–C(31)–C(32)	108.3(4)
P–C(7)–O(1)	116.0(3)	C(7)–O(1)–C(1)	119.4(4)

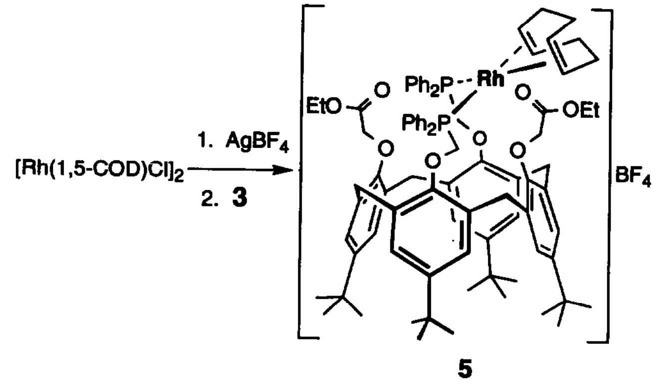
The ArCH_2 NMR signals are consistent with the presence of a calixarene moiety in a cone conformation (see Experimental part). The ^1J(PPt) coupling constant of 3536 Hz is typical for a *cis* geometry about the platinum atom [19]. The ^{31}P NMR (THF-C_6D_6) spectrum of the crude reaction mixture reveals the presence of small amounts (less than 5%) of a second platinum complex which was not isolated (^{31}P NMR signal at $\delta = 11.0$ ppm). The smaller *J*(PPt) coupling constant (2488 Hz) of this minor product as well as the observed chemical shift value [20] suggest that this product is the corresponding *trans* isomer. On gradually cooling a $CDCl_3$ solution of **4** from +50°C to −60°C, the ^{1}H NMR signals become broader, clearly showing that the molecule displays dynamic behaviour in solution. A collapse of the signals could not be reached in the observed temperature range, thus excluding the observation of slow conformer exchange. Molecular models suggest that for a *cis* isomer the strain is minimized when the platinum plane and the calixarene axis are not parallel. Note that the IR(KBr) spectrum of **4** displays two strong distinct absorption bands in the ester region (1757 and 1732 cm^{-1}) indicating that in the solid state the ester functions are asymmetrically located with respect to the platinum plane. These observations suggest that the dynamics associated with **4** result from an alternating restricted rotation of the metal plane around the P–P axis (see Fig. 2) leading to a fan-like motion of this plane. This movement involves limited internal rotations of both



2'

the Pt–P bonds and the O–C bonds of the O∩P substituents.

The ability of **3** to behave as a *cis* chelating ligand was also observed by reacting [Rh(1,5-cyclooctadiene) Cl] with 2 equiv $AgBF_4$ followed by treatment with 2 equiv **3** (eqn. (2)). This reaction leads to complex **5**. The *J*(PRh) coupling constant of 141 Hz indicates [21] a *cis* arrangement. As for complex **4**, the $ArOCH_2CO_2Et$ groups appear equivalent on the ^1H NMR time scale at room temperature. The signals become broader on decreasing the temperature, suggesting dynamics similar to those discussed above. Note that the ^{13}C NMR spectrum of **5**, measured at 25°C (see Experimental part), shows the non equivalence of the two $ArOCH_2CO_2Et$ moieties. This clearly establishes the loss of C_2 symmetry resulting from a coordination plane inclined with respect to the calixarene axis.



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(2)

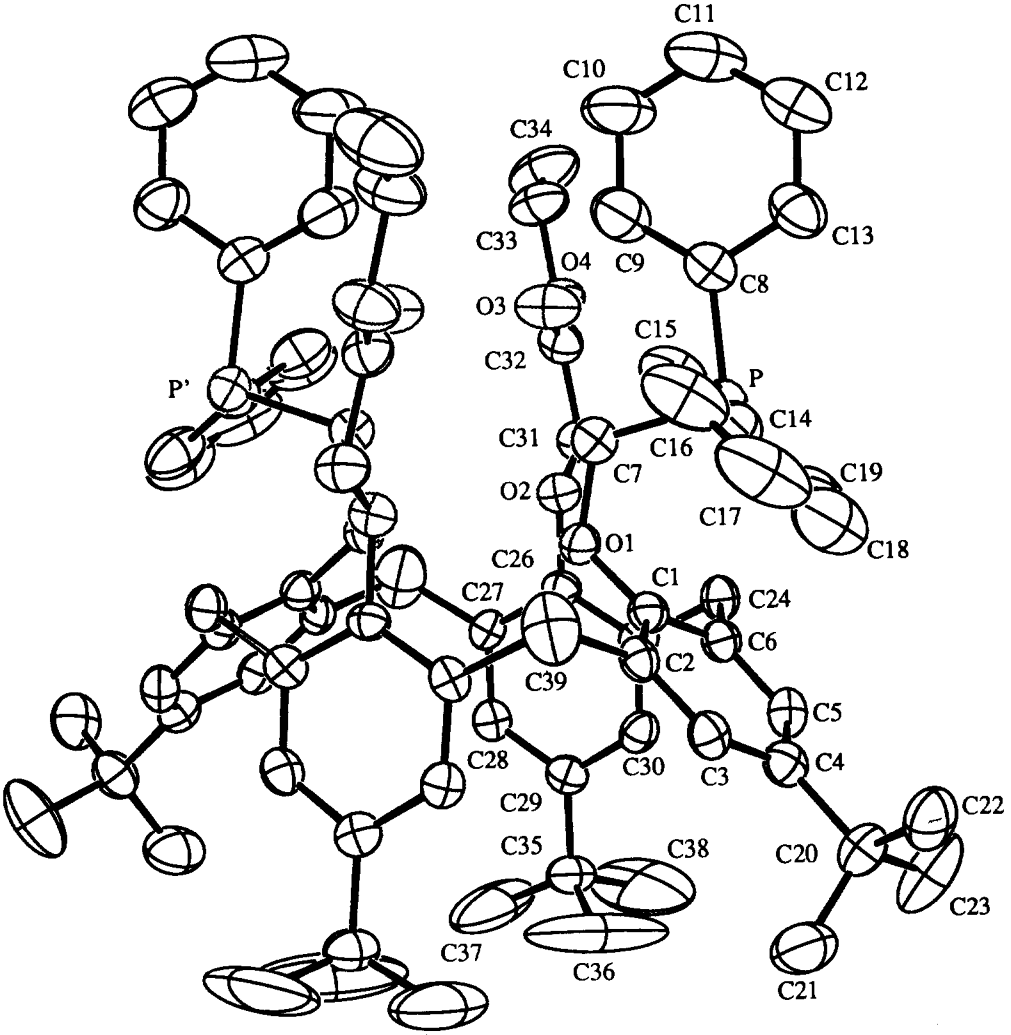
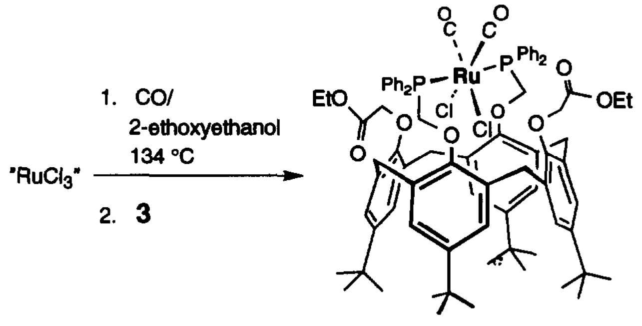


Fig. 1. ORTEP [24] representation of **3** showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of electron density. Hydrogen atoms are omitted.

The reaction of a boiling 2-ethoxyethanol solution of commercial ruthenium trichloride with carbon monoxide and subsequent addition of **3** quantitatively yielded complex **6** (eqn. (3)). The assignment of a *trans*-P,P stereochemistry for this complex is a result of a combination of IR and NMR measurements. The $^{31}P\{^1H\}$ NMR spectrum of **6** displays a single peak at 18.8 ppm. The IR (nujol) spectrum of **6** exhibits two strong $\nu(C{\equiv}O)$ absorption bands consistent with carbonyl ligands occupying relative *cis* positions [22].



6 (3)

As deduced from their signal in the $^{31}C\{^1H\}$ NMR spectrum (triplet at δ 192.39, $^2J(PC) = 9.5$ Hz), the carbonyl ligands are in a *cis* position with respect to the two equivalent phosphorus atoms [23]. These data unambiguously demonstrate the *trans* chelating behaviour of **3**. For steric reasons the carbonyl ligands are likely to point away from the cavity, whereas the chlorine ligands are directed towards the interior of the cavity. A variable ^1H NMR study revealed that all signals become larger on decreasing the temperature, indicating fluxional behaviour of **4**; however, no total broadening of the signals is to be observed above −50°C. Molecular models strongly suggest the possibility of a fast interconversion between the isomers shown in Fig. 3.

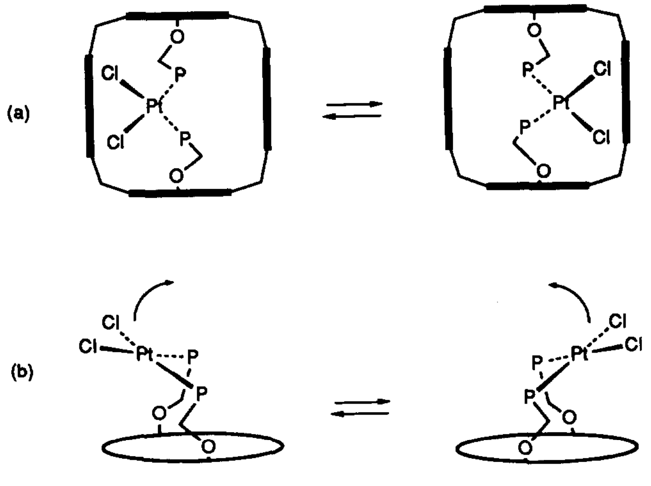


Fig. 2. Proposed dynamics of complex **4**: (a) view from the top; (b) view from the side.

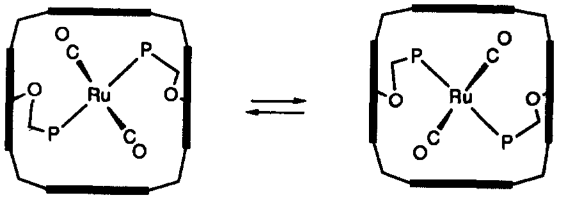


Fig. 3. Proposed dynamics in complex **6** (View from the top along the calixarene axis).

This process may be described as an alternating restricted rotation around the ruthenium atom of the P–Ru–P segment within a plane perpendicular to the calixarene axis. This motion which is reminiscent of a clockwork mechanism mainly involves limited internal rotation about the P–C(O) and C–O(Ar) bonds.

In conclusion, this work describes the first example of a diphosphane derived from a lower rim substituted calix[4]arene. This ligand which has C_2 symmetry was shown to be capable of chelating transition metals either in a *cis-P,P* or a *trans-P,P* fashion. This versatility reflects in particular the well known flexibility of cone conformers [24]. Further work will concentrate on the effects that a P_2,O_2-mixed-ligand environment may induce on the properties of transition metal centers.

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