Synthesis and characterisation of $PC_{sp^3}P$ phosphine and phosphinite platinum(II) complexes. Cyclometallation and simple coordination[†]

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New and improved preparative routes to the previously known PCP ligands *cis*-1,3-bis(diisopropylphosphinito)cyclohexane and *cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexane are reported. They react with 1 equivalent of dichloro(1,5-cyclooctadiene)platinum(II) [(COD)PtCl₂] to give the *cis* coordinated complex *cis*-[PtCl₂{*cis*-1,3-bis(di-isopropylphosphinito)}cyclohexane] and the C_{sp^3} -H activated complex *trans*-[PtCl{*cis*-1,3-bis(di-*tert*-butylphosphinio)}cyclohexane]. The new PCP ligand *cis*-1,3-bis(di-*tert*-butylphosphinito)cyclohexane]. The new PCP ligand *cis*-1,3-bis(di-*tert*-butylphosphinito)cyclohexane was synthesised and reacts with [(COD)PtCl₂] giving the di-nuclear *trans*-[PtCl₂{*cis*-1,3-bis(di-*tert*-butylphosphinito)cyclohexane}]₂, which is highly insoluble. All metal complexes were characterised with X-ray crystallography. DFT calculations indicate that the inability of the phosphinite ligands to cyclometallate is due to a kinetic barrier, possibly involving an axial–equatorial conformational change necessary for the C–H activation process.

Introduction

Transition metal complexes with PCP pincer ligands display a rich chemistry with many applications in homogeneous catalysis.¹ The strongly chelating nature of PCP ligands usually gives high thermal and oxidative stabilities to their transition metal complexes although it has been shown that there is decomposition at high temperatures giving highly active metal(0) species.² Most investigated are the complexes of $PC_{\mbox{\tiny sp}^2}P$ type but pioneering work by Shaw et al. describes the synthesis of numerous platinum-metal complexes of $PC_{sp^3}P$ type.³ We have also reported on the synthesis and catalytic applications of cyclohexyl based PCP ligands cis-1,3bis[(di-tert-butylphosphino)methyl]cyclohexane (1) and cis-1,3bis(di-isopropylphosphinito)cyclohexane (2).⁴ In particular ligand 2 behaved differently than the corresponding aromatic ligand and did not give cyclometallation with palladium(II). A number of complexes with aliphatic backbones have been described recently in both nickel⁵ and rhodium⁶ chemistry.

In this paper we further extend the family of PCP ligands with aliphatic cyclohexane backbones. The synthesis of the phosphinite ligand *cis*-1,3-bis(di-*tert*-butylphosphinito)cyclohexane **3** and desulfurisation of *cis*-1,3-bis[(di-*tert*-butylthiophosphoryl)methyl]cyclohexane **4** are described. Additionally, the coordination chemistry involving cycloocta-1,5-diene platinum dichloride [(COD)PtCl₂] and cyclohexyl based PCP ligands is presented. We also report on DFT calculations on these systems and provide a possible explanation for the different reactivity of phosphine and phosphinite based ligands.

Experimental

General procedures and materials

All experiments with metal complexes and the phosphine/phosphinite ligands were carried out under an atmosphere of nitrogen in a glovebox or using standard Schlenk or high vacuum-line techniques. Caution! Several reactions are performed in closed vessels at temperatures well above the boiling point of the solvent. This is a potential explosion hazard and should only be performed behind a blast shield using specially designed reaction vessels. We use glass (3.2 mm thick and tested for pressures up to 20 bar, giving a safe working pressure of ca. 10 bar) Strauss flasks equipped with 8 mm Kontes Teflon valves as described elsewhere.7 All non-deuterated solvents were vacuum-transferred from sodium benzophenone ketyl directly to the reaction vessel. Anhydrous CuCl₂ was obtained by keeping CuCl₂·2H₂O at 140 °C over night. Water used for washing in purification steps was degassed with N₂ for 2 h prior to use. KH in mineral oil was obtained from Aldrich and washed with hexane three times prior to use. All other commercially available reagents were purchased from Sigma Aldrich and used as received. Commercial cis, trans-1,3-cyclohexanediol consists of 55% cis and 45% trans according to ¹H NMR spectroscopy. The pure cis-isomer was obtained using a modified literature method,⁸ and gave a satisfactory ¹H NMR spectrum.9 [(COD)PtCl₂] was prepared according to the literature.10 $\,^1\mathrm{H},\,^{13}\mathrm{C}$ and $\,^{31}\mathrm{P}$ NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz (¹H). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (¹H and ¹³C NMR) or H₃PO₄ as reference. NMR multiplicities are abbreviated as follows: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, b = broad, v = virtual. Coupling constants for virtual triplets in ¹H and ¹³C NMR spectra are reported according to Cohen and Sheppard.¹¹ Elemental analyses were performed by H. Kolbe, Mülheim an der Ruhr, Germany.

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cis-1,3-Bis[(di-tert-butylphosphino)methyl]cyclohexane (1). A thick-walled Strauss-flask containing cis-1,3-bis[(di-t-butylthiophosphoryl)methyllcvclohexane 4 (0.31 g, 0.67 mmol) and LiAlH₄ (1.05 g, 27.7 mmol) was evacuated and THF (40 cm^3) was vacuumtransferred into the mixture. The flask was placed in an oil bath at 150 °C for 12 h before cooling to room temperature, releasing positive pressure of H_2S , purging with N_2 and withdrawing 0.6 cm³ for NMR analysis. Thus, five NMR samples were taken during the 3 d reaction time and after each test three freeze-pump-thaw cycles were carried out. The grey suspension was quenched by removal of THF and H₂S on the Schlenk line followed by addition of EtOAc (5.5 cm^3) and saturated Na₂SO₄ (aq) (5.5 cm^3) . THF (10 cm^3) was added for extraction and the clear, colour free organic solution was separated and dried over 4 Å molecular sieves. Removal of the solvent and drying the white sticky residue under vacuum gave pure 1. Yield 0.24 g (90%). ${}^{1}H$, ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectra were consistent with previous reports.4a

cis-1,3-Bis(di-isopropylphosphinito)cyclohexane (2). Method A. The literature procedure used for the corresponding *cis/trans* mixture was applied.^{4b} The crude reaction mixture was extracted with Et₂O and filtration followed by evaporation resulted in a yellow oil in almost quantitative yield according to ³¹P NMR spectroscopy.

Method B. To a THF solution (30 cm³) of *cis*-1,3-cyclohexanediol (0.58 g, 5.0 mmol), KH (0.40 g, 10.0 mmol) was slowly added and the solution was stirred for 14 h. Then a solution of ClPⁱPr₂ (1.6 cm³, 10.0 mmol) in THF (10 cm³) was added to the reaction mixture and it was stirred for another 17 h. The solvent was evaporated and the mixture was dissolved in ether and filtered. Removal of the ether afforded a colourless viscous oil which crystallised slowly upon standing. Yield: 1.25 g (72%). NMR data were consistent with those reported in the literature.⁴⁹

cis-1,3-Bis(di-tert-butylphosphinito)cyclohexane (3). Method A. A hexane solution of BuLi (1.6 M, 3.5 cm³, 5.6 mmol) was carefully added to an ice-cold THF (15 cm³) solution of cis-1,3cyclohexanediol (0.291 g, 2.51 mmol). The ice-bath was removed and the white suspension was allowed to stir for 2 h at room temperature, before being cooled down to 0 °C. A THF (15 cm³) solution of ClP'Bu₂ (1.00 cm³, 5.26 mmol) was added and the suspension was aged for 2 h at room temperature. The white suspension was heated at 160 °C overnight, which resulted in a pale yellow solution with a white solid after sedimentation. The organic phase was carefully separated using a cannula and the white solid was washed with a new portion of THF (10 cm³). The combined organic phases were evaporated, producing a semi-solid white residue. The residue was distributed between H_2O (10 cm³) and Et₂O (20 cm³), giving a pale yellow, transparent upper organic phase and a whitish somewhat cloudy water phase. The Et₂O was separated and the water phase extracted with another portion of Et_2O (10 cm³). The combined organic phases were dried with 4 Å molecular sieves over night. Filtration and evaporation of the solvent produced a waxy white residue. ³¹P NMR spectroscopy showed the product to be almost pure.

Method B. To a THF solution (30 cm³) of cis-1,3-cyclohexanediol (0.58 g, 5.0 mmol), KH (0.40 g, 10.0 mmol) was slowly added and the solution was stirred for 14 h. Then a solution of di-t-butylchlorophosphine (1.9 cm³, 10.0 mmol) in THF (10 cm³) was added to the reaction mixture and it was stirred for another 17 h. The solvent was evaporated, the mixture was dissolved in ether (75 cm³) and filtered. Removal of ether afforded a colourless viscous oil which crystallised slowly upon standing overnight. Yield: 1.80 g (89%). Anal. Calc. for C₂₂H₄₆O₂P₂: C, 65.32; H, 11.46; P, 15.31. Found: C, 65.18; H, 11.40; P, 15.26. ¹H NMR (C₆D₆) δ ppm: 0.81 (tq, 1H, $J_{H-H} = 14.0$ and $J_{P-H} = 3.5$ Hz, Cy), 0.95–1.15 (m, 2H, Cy), 1.08 and 1.10 (d, 36H, ${}^{3}J_{P-H} = 5.0$ Hz, *t*-Bu), 1.35– 1.45 (m, 2H, Cy), 1.95 (d, 2H, $J_{H-H} = 12.5$ Hz, Cy), 2.80 (d, 1H, $J_{\rm H-H} = 12.5$ Hz, Cy) and 3.50 (m, 2H, Cy). ¹³C NMR (C₆D₆) δ ppm: 20.84 (s, CH_2 , Cy), 27.73 and 27.61 (d, CH_3 , ${}^2J_{P-C} = 2.9$ Hz, *t*-Bu), 33.82 (d, CH_2 , ${}^{3}J_{P-C} = 4.4$ Hz, Cy), 34.83 and 34.63 (d, CH_2 , ${}^{3}J_{P-C} = 6.5$ Hz, Cy), 43.35 (vt, P–*C*(CH₃)₃, ${}^{1}J_{P-C} = 3.8$ Hz, *t*-Bu), 78.91 (d, P–O–CH, ${}^{2}J_{P-C} = 18.2$ Hz, Cy). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆) δ ppm: 153.9 (s). ${}^{31}P{}^{1}H{}$ NMR (THF-d₈): δ 153.5 (s).

cis-[PtCl₂{*cis*-1,3-bis(di-isopropylphosphinito)cyclohexane}] (5). In a glovebox, 2 (0.48 g, 1.37 mmol) was added to a pale grey suspension of [(COD)PtCl₂] (0.52 g, 1.38 mmol) in THF (40 cm³) at room temperature. Within minutes the reaction mixture turned to a pale yellow solution and a ³¹P NMR spectrum confirmed that no starting material was present in the solution. Evaporation of the solvent and recrystallisation from THF–heptane (1 : 1) gave crystals suitable for X-ray diffraction. Yield 0.61 g (72%).

Anal. Calc. for $C_{18}H_{38}Cl_2O_2P_2Pt: C, 35.19; H, 6.23.$ Found: C, 35.27; H, 6.19. ¹H NMR (THF-d₈): $\delta = 0.90$ (m, 1H, Cy), 0.96, 1.23, 1.35, 1.63, (dd, 24H, ${}^{3}J_{P-H} = 7.0$ Hz and ${}^{3}J_{H-H} = 16.7$ Hz, i-Pr Me), 1.00 (m, 2H, Cy), 1.25 (m, 2H, Cy), 1.45 (m, 2H, Cy), 1.70 (m, 2H, Cy), 2.45 (m, 2H, *i*-PrCH), 3.25 (m, 4H, Cy and *i*-Pr). ${}^{13}C{}^{1}H$ } NMR (THF-d₈): $\delta = 16.78$ (s, CyCH₂), 18.42, 19.76, 21.53 (s, *i*-Pr CH₃), 29.49 and 32.98 (d, CH₂, ${}^{3}J_{P-C} = 4.9$ Hz, Cy), 32.02 (vt, CH, ${}^{3}J_{P-C} = 3.3$ Hz, *i*-Pr), 71.50 (d, ${}^{2}J_{P-C} = 20.1$ Hz, P-O-CH). ${}^{31}P{}^{1}H$ } NMR (THF-d₈): $\delta = 111.60$ (${}^{1}J_{P-Pt} = 4028$ Hz).

trans-[PtCl₂{*cis*-1,3-bis(di-*t*-butylphosphinito)cyclohexane}]₂ (6). To a colourless solution of 3 (0.25 g, 0.62 mmol) in THF (15 cm³), [(COD)PtCl₂] (0.23 g, 0.62 mmol) was added and the mixture was heated at 150° C overnight without stirring. Yellow crystals were formed, and the crystals were filtered off and washed with hexane (5 cm³), methanol (10 cm³) and ether (5 cm³) and dried. Yield: 0.36 g (86%). Anal. Calc for $C_{45}H_{96}Cl_4O_5P_4Pt_2$: C, 39.36; H, 7.05; P, 9.02. Found: C, 39.25; H, 7.08; P, 9.18

trans-[PtCl{*cis*-1,3-bis(di-*tert*-butylphosphino)cyclohexyl}] (7). In a glovebox, 1 (0.31 g, 0.78 mmol) was added to a pale grey suspension of [(COD)PtCl₂] (0.29 g, 0.77 mmol) in THF (40 cm³) in a Strauss-flask. The flask was put in an oil-bath and at 140 °C a pale yellow solution resulted. After 30 min at 140 °C the reaction solution was allowed to cool down to room temperature. Evaporation of the solvent and recrystallisation from pentane gave crystals suitable for X-ray diffraction. Yield 0.30 g (63%). Anal. Calc for C₂₄H₄₉ClP₂Pt: C, 45.75; H, 7.84; P, 9.83. Found: C, 45.83; H, 7.79; P, 9.76. ¹H NMR (THF-d₈): δ 0.90–2.10 (m region, CH & CH₂), 1.38 (vt, ³J_{PH} = 13.2 Hz, 18H, C(CH₃)₃), 1.42 (vt, ³J_{PH} = 13.3 Hz, 18H, *t*-Bu). ¹³C{¹H} NMR (C₆D₆): δ 27.8 (t, ⁴J_{PC} = 1.4 Hz), 29.7 (vt, ²J_{PC} = 5.5 Hz, C(CH₃)₃), 30.2 (vt, ²J_{PC} = 5.3 Hz,

Table 1Crystal data for 5, 6 and 7

	5	6	7
Formula	$C_{18}H_{38}Cl_2O_2P_2Pt$	$C_{45}H_{96}Cl_4O_5P_4Pt_2$	C ₂₄ H ₄₉ ClP ₂ Pt
Fw	614.41	1373.08	630.11
Space group	Pbca	C2/c	$P2_1/n$
a/Å	12.8734(8)	28.8263(11)	12.0176(8)
b/Å	14.8662(9)	8.7302(2)	14.8027(9)
c/Å	24.0444(13)	44.3883(10)	15.7279(9)
$\beta/^{\circ}$	90	96.065(3)	100.786(5)
$V/Å^3$	4601.6(5)	11108.2(6)	2748.5(3)
Z	8	8	4
Dcalcd/g cm ⁻³	1.774	1.642	1.523
μ/mm^{-1}	6.480	5.379	5.327
θ range/°	2.26-32.89	2.21-32.77	2.21-32.72
No. reflns collected	43 390	40 857	24 21 5
No. of unique reflns	8030	17 354	9275
No. of reflns $I > 2\sigma(I)$	3388	4742	4711
$R(F) (I > 2\sigma(I))^a$	0.0607	0.0586	0.0347
$wR2(F^2)$ (all data) ^b	0.1481	0.1724	0.0878
S^c	0.925	0.735	0.984
Rint	0.1426	0.0721	0.0410

C(CH₃)₃), 33.8 (vt, $J_{PC} = 24.5$ Hz), 34.3 (vt, ${}^{2}J_{PC} = 20.2$ Hz), 36.9 (vt, ${}^{3}J_{PC} = 20.9$ Hz), 36.8 (vt, ${}^{3}J_{PC} = 16.9$ Hz), 48.8 (s, ${}^{1}J_{C-Pt} = 730$ Hz, HC–Pt), 50.8 (vt, ${}^{2}J_{PC} = 14.7$ Hz). ${}^{31}P{}^{1}H$ NMR (C₆D₆): δ 63.9 (s, $J_{P-Pt} = 3127$ Hz).

with Raney-nickel or trichlorosilane have been unsuccessful¹⁶ and we decided to use LiAlH₄ in THF. The reaction of **4** with LiAlH₄ in THF at 150 °C over 3 d gave **1** as a single product with H_2S as a by-product, *cf*. Scheme 1.

Crystallography[†]

Intensity data were collected with an Oxford Diffraction Xcalibur 3 system using ω -scans and Mo-K α ($\lambda = 0.71073$ Å) radiation.¹² Intensity data were extracted and integrated using Crysalis RED.¹³ The structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.¹⁴ Non-H atoms were refined with anisotropic displacement. All hydrogen atoms were constrained to parent sites, using a riding model. Crystal data and details about data collection are given in Table 1.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712660c

DFT calculations

The geometries of the model compounds were optimised using B3LYP DFT implemented by the programme Jaguar¹⁵ with the lav3p basis set and electronic energies were calculated. Starting geometries were obtained from the crystal structures of **5** and **7**.

Results

Reduction of

1,3-cis-bis[(di-tert-butylthiophosphoryl)methyl]cyclohexane (4)

In previous syntheses of ligand 1 the purification and identification of the product was hampered by the oxygen sensitivity of this diphosphine and hence it has been converted to the corresponding phosphine sulfide, which was isolated and fully characterised.^{4a} Previous attempts to cleanly remove the sulfur on the PCP ligand



The reaction was conveniently monitored using ³¹P NMR spectroscopy, and at the same time the excess hydrogen sulfide was ventilated from the reaction mixture. In accordance with previous work^{4a} the starting material and product display singlets at $\delta = 76.3$ and 20.7 ppm, respectively, in ³¹P NMR spectra with THF-d₈ as the solvent. Monitoring the reaction mixture also revealed the presence of the mono-sulfurated intermediate *cis*-(1-di-*tert*-butylthiophosphorylmethyl-3-di-*tert*-butylphosphinomethyl)cyclohexane (**8**) seen as two peaks in a 1 : 1 ratio at $\delta = 76.6$ and 20.4 ppm. The reaction progress shows typical intermediate behaviour of **8**, where it accumulates to approximately 60% and then disappears again. After 100 h the reaction is complete and compound **1** was obtained in excellent yield and high purity through a simple work-up procedure.

Synthesis of phosphinite ligands 2 and 3

The *cis* isomer of 1,3-cyclohexanediol was separated from the commercially available *cis/trans* mixture according to the protocol

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of Lehtonen *et al.*,⁸ involving complexation with anhydrous $CuCl_2$ followed by liberation of the *cis*-diol by treatment with gaseous NH₃. To generate *cis*-1,3-bis(di-isopropylphosphinito)-cyclohexane (**2**) and *cis*-1,3-bis(di-*tert*-butylphosphinito)cyclohexane (**3**) the synthetic strategy of Sjövall *et al.* was initially used.^{4b}

Treating cis-1,3-cyclohexanediol with n-BuLi gave the corresponding alkoxides that readily reacted with $ClP'Pr_2$ and $ClP'Bu_2$, respectively, affording the phosphinite PCP ligands 2 and 3 in sufficient purity according to ³¹P NMR spectroscopy, cf. Scheme 2. A remarkable difference in reactivity was observed between these two chlorophosphines. When ClPⁱPr₂ was mixed with the alkoxide at 0 °C the reaction started instantaneously as indicated by the fact that the reaction suspension slowly turned into a solution as the reaction mixture reached room temperature. Contrary to this, the reaction of ClP'Bu₂ with the alkoxide required an elevated temperature to start and was only driven to completeness at 160 °C, as indicated by ³¹P NMR spectroscopy. When using n-BuLi as a deprotonation agent both phosphinite products were tedious to purify and the product mixtures never reached analytical purity. Continued purification also resulted in a large decrease in yield and was always stopped when the ³¹P NMR spectrum showed satisfactory purity. Using KH as the deprotonation agent giving the potassium salts of the diol instead of the lithium salts was a superior method. The potassium chloride formed during the reaction was easily separated by dissolving the reaction mixture in ether and filtering. Thus, ligands 2 and 3 were isolated in a good yield and fully characterised, with the ³¹P NMR spectrum of ligand 2 consistent with that reported in the literature.^{4b}



Reaction of ligands 2 and 3 with $[(COD)PtCl_2]$

When a THF solution of **2** was added to a THF suspension of [(COD)PtCl₂] at room temperature the platinum precursor dissolved within minutes, *cf.* Scheme 3. This resulted in a pale yellow solution, which was analysed by ³¹P NMR spectroscopy 5 min after mixing. The spectrum revealed total consumption of **2** and evaporation of the solvent and recrystallisation from boiling THF–heptane 1 : 1 yielded complex **5** as air-stable, colourless crystals. The ³¹P{¹H} NMR spectrum in THF-d₈ gives rise to a singlet at $\delta = 111.6$ ppm with a ¹J_{PtP} of 4028 Hz, indicating a *cis* geometry. The *cis* coordination mode has earlier been observed for the iodo-palladium analogue.⁴⁶ X-Ray diffraction of the crystals of **5** confirmed the *cis*-structure with a diaxial arrangement of the cyclohexyl ring. A perspective view of the molecular structure is shown in Fig. 1 including selected bond lengths and angles.



Fig. 1 DIAMOND drawing of 5 at the 30% probability level. Most hydrogens and the methyl carbons on the *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pt–Cl1 2.374(2), Pt–Cl2 2.370(2), Pt–P1 2.238(2), Pt–P2 2.234(2), Pt···C1 3.922(9), Cl1–Pt–Cl2 86.96(8), P1–Pt–P2 100.59(8), Cl1–Pt–P1 88.01(8), Cl2–Pt–P2 84.45(7).

The structure exhibits a distorted *cis* square-planar geometry. Due to the rigid structure of the cyclohexane ring the chelate causes slight deformation of the complex giving a P1–Pt–P2 angle of $100.59(8)^{\circ}$. This is somewhat larger than the earlier reported palladium iodine analogue^{4b} and deviation is in general expected in an eight-membered ring with a naturally large bite angle. The diaxial substitution pattern on the cyclohexane ring causes the ring to be positioned well above the plane of the complex and the cyclohexane ring adopts the chair conformation, where the bond angles compare fairly well to those in free cyclohexane (111.5°).¹⁷

Intramolecular hydrogen bonding is present between three of the isopropyl hydrogens and two of the chlorines (Cl2– H9 2.726(2) Å; Cl1–H8 2.724(2) Å; H10–Cl2 2.961(2) Å). Our initial aim to activate the C1–H bond had not been achieved. It can be noted that the Pt–C1 distance is 3.92 Å, which is far from an agostic interaction. Attempts to induce C–H activation by using elevated temperature, treatment with silver triflate or triethyl amine were not fruitful. Addition of silver triflate gave immediate precipitation of silver chloride but the ³¹P NMR spectrum indicated formation of several products none of which was the desired cyclometallated product. Filtration through Celite and heating did not enrich any possible product. Treating **5** with triethyl amine in an effort to deprotonate C1 had absolutely no effect nor had a heating of the complex overnight at 125 °C. In conclusion, trying to convert *cis* coordinated complex **5** to a *trans*, C–H activated complex seems unfeasible. Ligand **2** apparently prefers a diaxial conformation whereas C–H activation seems to demand a diequatorial conformation.

Reaction of [COD]PtCl₂ with the *t*-butyl analogue 3 in THF at 150° C afforded a material, which was not soluble in any of the common organic solvents, precluding an NMR characterisation. When the reaction was carried out without stirring, air-stable, yellow crystals, which were filtered off and washed with methanol and ether, were obtained. These were also insoluble but the quality of the crystals enabled a single crystal X-ray diffraction experiment and they were also characterised by elemental analysis. A perspective view of the molecular structure is shown in Fig. 2. The structure shows that there is no cyclometallation on the C1 carbon of the ligand and the complex obtained is a dimer in which the platinum coordinates to two trans oriented phosphorus atoms from two different ligands. The average Pt-P distance is 2.324 (3) Å and the average P-Pt-P angle is 176.6 (9)°. Also the two chlorine atoms bonded to the platinum are trans to each other. The Pt-Cl bond distances vary dramatically from 2.298(4) to 2.382(4) Å and the average Cl–Pt–Cl angle is 158.8 $(3)^{\circ}$, strongly deviating from the expected 180°. The overall geometry around the metal centre is distorted square-planar. A similar type of complex has been observed in the case of palladium using the isopropyl ligand 2.4b We believe that the formation of a dinuclear complex instead of a mononuclear one as in the case of the isopropyl analogue is due to steric constraints. By adopting the structure shown in Fig. 2 the two bulky phosphine substituents can be trans oriented and equatorial although no cyclometallation is obtained. Together the 16-membered ring forms a cage like structure with a methanol (from the washing) as a guest. This methanol shows a disorder as indicated by the unreasonably long C-O distance; any attempt to resolve it failed. From a packing diagram it can be seen that the cages form a tunnel-like structure along the b axis. However, from a space-filling plot it is clear that the cage is accessible only from one side, viz. the top side in the representation in Fig. 2.

Fig. 2 DIAMOND drawing of compound **6** at the 30% probability level. Hydrogen atoms and methyl carbons on the *t*-butyl groups are omitted for clarity. Note the disordered methanol in the cavity formed by the 16-membered ring. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pt1–Cl1 2.382(4), Pt1–Cl2 2.298(4), Pt2–Cl3 2.301(7), Pt2–Cl4 2.335(5), Cl1–Pt–Cl2 158.25(19), Cl3-Pt2–Cl4 159.3(3).

Reaction of ligand 1 with [(COD)PtCl₂]

When a THF solution of phosphine ligand 1 was added to a THF suspension of [(COD)PtCl₂] at room temperature no dissolution of the platinum precursor was observed. To obtain a reaction demanded a temperature of 140 °C. This differs substantially from the phosphinite complexation. By increasing the temperature in small steps an intermediate was observed when monitoring the reaction by ³¹P NMR spectroscopy. The intermediate was observed as a singlet ($\delta = 37.4$) with satellites ($J_{PtP} = 4282$ Hz). It was not isolated and disappeared upon further heating but we strongly suspect it to be the cis coordinated complex 9, cf. Scheme 3. Continued heating of the THF mixture of 1 and [(COD)PtCl₂] at 140 °C for 30 min resulted in a pale yellow solution containing only compound 7. No base was needed to induce cyclometallation and, interestingly, 7 is robust in a THF solution at 140 °C with one equivalent of HCl. Compound 7 gives rise to a ³¹P NMR resonance at 63.9 ppm with a ${}^{1}J_{Pt-P}$ of 3127 Hz indicating a *trans* geometry. The cyclometallation is also substantiated in the ¹³C NMR spectrum where the C1 resonance comes at 48.8 ppm with platinum satellites (${}^{1}J_{Pt-C} = 730$ Hz). Our conclusions from the NMR investigation were unambiguously confirmed by an X-ray crystallographic analysis. A perspective view of the molecular structure is shown in Fig. 3 including selected bond lengths and angles.



Fig. 3 DIAMOND drawing of compound **7** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pt1–C1 2.065(4), Pt1–Cl1 2.434(2), Pt1–P1 2.303(3), Pt1–P2 2.308(5), P1–Pt1–P2 167.61(4).

The structure displays a distorted square-planar geometry with the phosphorus atoms located nearly trans to each other. The P1-Pt1-P2 angle of 167.61(4)° illustrates the distortion caused by the chelate, forcing the two phosphines to pinch back, away from the chlorine. The Pt-Cl bond is unusually long at 2.434(2) Å, illustrating the high trans influence of the cyclohexyl ring. The cyclohexane ring adopts the chair conformation and is aligned with the plane of the complex, with the activated C-H bond in an equatorial position. Similar to complex 5 there is seemingly very little strain in the ring backbone. Confirming the observation in solution the molecules has C_s -symmetry with a mirror plane involving Cl1, Pt1, C1 and C4. Thus the ¹³C{¹H} NMR spectrum contains nine unique resonances with the tert-butyl groups above and below the coordination plane being magnetically inequivalent. This is observed in both the ¹H (Δ 19.0 Hz) and ¹³C{H} (Δ 68.9 Hz) NMR spectra.

DFT calculations

To shed some light on the inability of ligands 2 and 3 to cyclometallate we decided to study some model reactions using DFT calculations. There are always errors in trying to calculate enthalpies or free energies but by looking at the energy difference between two similar reactions, those of ligands 1 and 3, the errors are minimised. The reactions studied are shown with their energies in Scheme 4.





By calculating the electronic energies for the six compounds two $\Delta\Delta E$ values were obtained and in both cases the reaction is 2 kcal mol⁻¹ more exothermic in the phosphine case as compared to the phosphinite case. This indicates, as experimentally observed, that there is a small thermodynamic preference for the cyclometallation of **1**. However, the differences both in coordination of the ligands and in the actual cyclometallation are small and the inability of **2** and **3** to cyclometallate is probably based on things other than an unfavourable equilibrium.

Discussion

The present cyclometallation reactions are C–H activations with a concerted mechanism (either electrophilic or oxidative addition)¹⁸ and it comes as no surprise that the C(sp³)–H bond with its higher p-character is more difficult to activate than the corresponding C(sp²)–H bond.¹⁹ It is plausible that ligand **1** is coordinated in a *cis* diaxial manner in intermediate **8**²⁰ and that activation then takes place at an equatorial C–H bond with both phosphine arms in an equatorial conformation.

This conformational change brings the C–H bond into the vicinity of the metal centre as shown in Scheme 5. The calculations indicate that there is a kinetic barrier towards cyclometallation of the phosphinite ligands. However, both inter- and intramolecular C–H activations are usually favoured by electrophilic metal centres, which facilitate coordination and in this respect we would have expected the phosphinites to favour cyclometallation. Interestingly, this is also observed for a straight chain aliphatic



Scheme 5

phosphinite ligand which has been reported to easily give pincer complexes with Ni(II).^{5b} This leads us to the conclusion that it is the axial–equatorial flip in the present system and the corresponding palladium system^{4b} that gives rise to an unusually large barrier in the phosphinites. Due to the strain of the cyclohexyl ring the conformational change in **9** is probably on the verge of what is possible and the shorter bond distances in the phosphinites completely inhibit the ring flip.²¹

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