

Synthesis, characterisation and catalytic investigation of a new type of PC(sp³)P pincer Pd(II) complex

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Received 17th December 2001, Accepted 13th February 2002
First published as an Advance Article on the web 11th March 2002

The diphosphine *cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexane (**2**) has been synthesised and its complexation in palladium chemistry has been investigated. Ligand **2** is capable of tricoordination, for instance as demonstrated by an X-ray crystal structure determination of the complex [Pd(**2**)I], and it is a rare example of a PC(sp³)P pincer ligand. A catalytic study of the Heck reaction revealed that the bis-chelated complex [Pd(**2**)(CO₂-CF₃)] is a highly active, air-stable precatalyst in the olefination of iodo- and bromo-benzenes. It is evident that, in comparison with the analogous aromatic PC(sp²)P system, by switching the hybridisation of the central carbon donor atom from sp² to sp³ improvement in terms of catalytic activity is achieved.

Introduction

Ever since the first examples of metallation of aliphatic and aromatic hydrocarbons a considerable amount of experimental and theoretical work has been carried out to enable an understanding of the main features of the process.¹ Today an impressive number of metallacyclic complexes have been synthesised especially *via* intramolecular C–H activation.² Since the pioneering work by Lewis *et al.* more than a decade ago,³ such metallacyclic complexes are now emerging as a new family of precatalysts in organometallic homogeneous catalysis.⁴ In this context, the two most well studied ligand systems are the metallacyclic compounds derived from tris(*o*-tolyl)phosphines⁵ and PCP-type ligands.⁶ The latter ligand results in a complex which is characterised by a rigid molecular backbone with an extensive hydrophobic cavity surrounding the transition metal, sometimes promoting both unusual coordination geometry⁷ and unique chemical reactivity.⁸ The PCP complexes have shown to be excellent or outstanding as catalyst precursors for a wide range of metal-mediated organic transformations including dehydrogenation,^{6a,b} Kharasch addition,^{6c,d} ketone reduction,^{6e} asymmetric aldol,^{6f,g} and Heck reactions.^{6h-k} The syntheses of the analogous SCS and NCN pincer complexes, along with their catalytic capacity, have also recently been reported.⁹

The overwhelming majority of the reported PCP pincer complexes are based on the same structural principle, namely a bis-chelating metallacycle incorporating an aromatic carbon formed by C–H activating a 1,3-bis(phosphinomethyl)benzene moiety. Although this is also applicable to saturated carbons only a few aliphatic PCP ligands have been reported,¹⁰ and catalytic properties of such compounds have generally not been examined. Importantly, it has been suggested that there might be a substantial effect on the catalytic activity of a metallacyclic complex by changing the identity of the carbon donor atom of the phosphine ligand from an aromatic to an aliphatic carbon.¹¹

In this paper we report the synthesis of *cis*-1,3-(^tBu₂PCH₂)₂C₆H₁₀ (Chart 1), which is the strict aliphatic analogue to 1,3-bis(phosphinomethyl)benzene, and its palladium coordination chemistry. It will be shown that **2** constitutes a rare example of a ligand capable of PC(sp³)P chelation. The aliphatic pincer complex synthesised herein was examined as a precatalyst in the Heck reaction with iodo- and bromo-benzenes. It is a highly active catalyst and it adds further

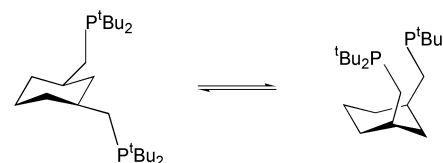


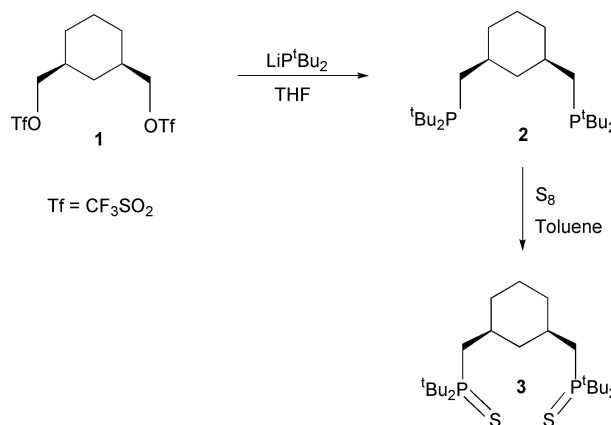
Chart 1

validation to the suggestion that catalytic enhancement can be realised by switching from an aromatic to an aliphatic central donor carbon atom in a tridentate PCP catalyst.

Results and discussion

Ligand synthesis

The diphosphine *cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexane (**2**) was prepared by careful addition of *cis*-1,3-bis[(trifluoromethylsulfonyloxy)methyl]cyclohexane (**1**) to a cooled (–60 °C) THF solution containing lithium di-*tert*-butylphosphide (Scheme 1). According to ³¹P{¹H} NMR spectroscopy the reaction was essentially clean and further purification of the air-sensitive compound **2** was thus not necessary. However, in order to obtain an elemental analysis, **2** was reacted with S₈ in toluene to give the air-stable compound *cis*-1,3-bis[(di-*tert*-butylthiophosphoryl)methyl]cyclohexane (**3**)

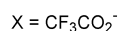
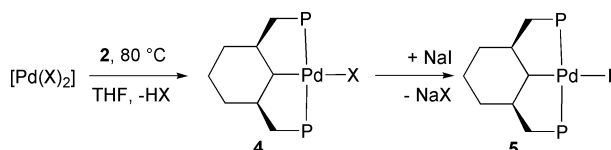


Scheme 1

(Scheme 1), which was fully characterised. The C_s configured compounds **2** and **3** display four sets of signals originating from the cyclohexane carbons in their respective $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and the phosphorus atoms are displayed as singlets at 20.9 (**2**) and 76.5 ppm (**3**), respectively, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

Complexation

When a THF solution of the palladium complex $[\text{Pd}(\text{CO}_2\text{CF}_3)_2]$ and 1 equivalent of **2** was stirred for 1 hour at 80 °C, direct palladium insertion into one of the C–H bonds of the sp^3 hybridised C2 ring-carbon took place, resulting in complex **4** (Scheme 2). The outcome of the reaction is opposite to what was



Substituents on P atoms are omitted

Scheme 2

found for the analogous phenyl substituted diphosphine *cis*-1,3- $(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_{10}$, which gives the complex *cis*- $[\text{Pd}(\text{cis}\text{-}1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_{10})(\text{CO}_2\text{CF}_3)_2]$ enabled by the diaxial orientation of the cyclohexane substituents.¹² Interestingly, this connection between C–H activation ability and phosphorus atom substituents is not found for the fully analogous aromatic phosphines, which are known to cyclometallate readily with transition-metal centres.¹³

The weakly coordinated trifluoroacetato ligand in **4** is easily substituted and anion metathesis employing an excess of NaI in THF afforded complex **5** cleanly (Scheme 2). Both these complexes were fully characterised by multinuclear NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit singlets at 71.7 (**4**) and 70.5 ppm (**5**). Such significant downfield shifts compared to the shift for the free ligand is in accordance with the five-ring chelation effect.¹⁴ In addition, in both $^{13}\text{C}\{^1\text{H}\}$ NMR spectra a triplet is displayed further downfield than expected for a simple aliphatic carbon (at 60.1 ppm ($^2J_{\text{PC}} = 2.9$ Hz) for **4** and 72.3 ppm ($^2J_{\text{PC}} = 5.2$ Hz) for **5**). $^{13}\text{C}\{^1\text{H}\}$ DEPT NMR experiments verified these signals to originate from a methine carbon, namely the cyclometallated central donor atom of the $\text{PC}(\text{sp}^3)\text{P}$ ligand.

In order to unambiguously determine which C–H bond on the C2 ring carbon has been cleaved by the palladium centre an X-ray crystallographic analysis of **5** was carried out. Colourless blocks suitable for X-ray crystallography were grown from a pentane solution at –18 °C. A perspective view of the molecular structure is shown in Fig. 1,¹⁵ including selected bond distances and angles.

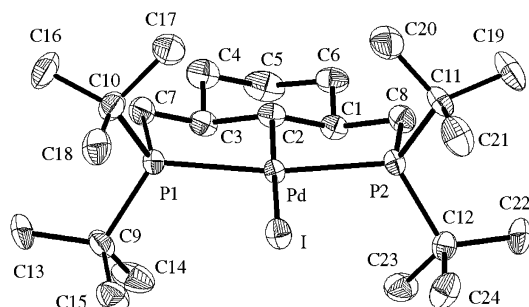


Fig. 1 A DIAMOND plot of complex **5**. Bond distances (Å) and angles (°) with estimated standard deviations: Pd–P1 = 2.332(1); Pd–P2 = 2.335(1); Pd–C2 = 2.108(5); Pd–I = 2.7252(6); P1–Pd–P2 = 166.2(5); P1–Pd–C2 = 83.7(1); P2–Pd–C2 = 82.7(1); C2–Pd–I = 174.9(1).

Complex **5** exhibits a distorted square-planar geometry with the phosphorus atoms located nearly *trans* to each other. The P1–Pd–P2 (166.2(5)°) angle is identical to and the Pd–P1 (2.332(1) Å), Pd–P2 (2.335(1) Å) and Pd–C2 (2.108(5) Å) bond distances are close to the ones observed in the related aliphatic pincer complex $[\text{Pd}\{\text{CH}_3\}\{\text{tBu}_2\text{PCH}_2\text{CH}_2\text{CHCH}_2\text{-CH}_2\text{P}^t\text{Bu}_2\}]$.^{10b} The pinching away of the two P atoms from the iodo ligand results in acute angles for the bis-chelating system (P1–Pd–C2 = 83.7(1)°, P2–Pd–C2 = 82.7(1)°). The chelate system adopts a double-bent conformation with a bisecting perpendicular pseudo-mirror plane (Fig. 2).¹⁵ Five of the atoms

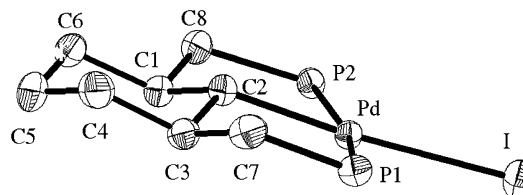
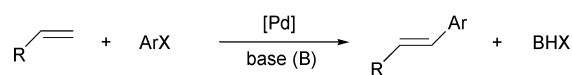


Fig. 2 A DIAMOND plot showing the double-bent conformation of the bis-chelate in complex **5**, as well as the chair conformation of the cyclohexane skeleton. Bond angles (°) with estimated standard deviations: C1–C2–C3 = 111.2(4); C2–C3–C4 = 109.8(4); C3–C4–C5 = 111.6(5); C4–C5–C6 = 111.6(5); C5–C6–C1 = 111.9(5); C6–C1–C2 = 111.5(4).

in the $\text{PC}(\text{sp}^3)\text{P}$ ligand (P1, P2, C2, C7 and C8) are almost situated in the plane of the complex with the displaced methine groups C1 and C3 pointing away in the same direction. This arrangement results in magnetically different environments above and below the square-plane, which is also manifested in solution with dual resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** for the *tert*-butyl substituents on the phosphorus atoms. The cyclohexane ring adopts the chair conformation and is aligned with the plane of the complex, with the equatorial C2–H bond being activated (Fig. 2). There is almost no built-in strain in the cyclohexane ring, which is reflected by its endocyclic bond angles; only the C2–C3–C4 angle (109.8(4)°) deviates substantially from free cyclohexane (111.5°).¹⁶

Catalysis

The palladium-catalysed vinylation of aryl halides, the so-called Heck reaction, is one of the most important methods for generating new C–C bonds (Scheme 3).¹⁷ Although numerous



Scheme 3

$\text{Pd}(0)$ and $\text{Pd}(\text{II})$ precursor complexes can mediate this reaction palladacycles are among the most reactive precatalysts reported to date.¹⁸ The key features for many long-lived catalysts applied in Heck chemistry are the stabilising effects imposed by chelation and/or steric shielding of the transition-metal centre enabling long reaction times at high temperatures. The congested complexes **4** and **5** fulfill these requirements and we considered undertaking a catalytic study of the Heck reaction.

An impressive number of different highly active precatalysts have appeared in the literature.¹⁹ Thus, it has been shown that arylation of olefins with iodo- and bromo-benzenes can be run with very low loads of catalyst (aryl halide to catalyst ratios ranging from 10^5 to 10^6) which, along with high yields of product (often >90%), means that high to huge turnover numbers (TON) can be reached. In our study on the catalytic properties of complexes **4** and **5** we have carefully chosen substrates, reaction conditions and product yields in order to be able to do just comparisons with literature values.

As shown in Table 1, complex **4** is indeed a very active catalyst in the arylation of alkenes with aryl iodides and bromides.²⁰

Table 1 Results of the Heck reaction mediated by catalyst precursor **4** under various reaction conditions including some literature values

Entry	ArX ^a /mmol	Olefin ^b /mmol	Solvent	Base ^c	[Pd]/mmol	t/h	T/°C	TON ^d	TOF ^e /h ⁻¹	Yield ^f (%)
1	PhI (6)	mac (7.5)	NMP	Na ₂ CO ₃	6 × 10 ⁻⁵	14	140	100 000	7 140	100
2	PhI (6)	mac (7.5)	NMP	NaOAc	6 × 10 ⁻⁵	14	140	69 750	4 980	70
3	PhI (6)	mac (7.5)	NMP	NBu ₃	6 × 10 ⁻⁵	14	140	16 100	1 150	16
4	PhI (6)	mac (7.5)	DMF	Na ₂ CO ₃	6 × 10 ⁻⁵	14	140	77 400	5 530	77
5	PhI (6)	mac (7.5)	DMAc	Na ₂ CO ₃	6 × 10 ⁻⁵	14	140	72 500	5 180	72
6	PhI (12)	mac (14)	NMP	Na ₂ CO ₃	3.5 × 10 ⁻⁵	45	140	332 500	7 390	97
7	PhI (12)	mac (14)	NMP	Na ₂ CO ₃	2 × 10 ⁻⁵	77	140	534 000	6 935	89
8 ^g	PhI (50)	mac (60)	NMP	Na ₂ CO ₃	8.75 × 10 ⁻⁵	350	140	520 500	1 490	91
9 ^h	PhI (6)	sty (7.5)	NMP	Na ₂ CO ₃	3 × 10 ⁻⁵	48	140	190 200	3 960	95
10	PhI (12)	bac (14)	NMP	Na ₂ CO ₃	4 × 10 ⁻⁵	46	160	282 400	6 150	94
11 ^g	PhI (5)	bac (6)	NMP	Na ₂ CO ₃	3.5 × 10 ⁻⁵	88	160	108 000	1 230	77
12	4-bba (6)	mac (7.5)	NMP	Na ₂ CO ₃	3.5 × 10 ⁻⁵	49	160	149 100	3 040	87
13	PhBr (6)	mac (7.5)	NMP	Na ₂ CO ₃	3.5 × 10 ⁻⁵	90	160	140 600	1 560	82

^a 4-bba = 4-Bromobenzaldehyde. ^b mac = Methyl acrylate, bac = *n*-butyl acrylate, sty = styrene. ^c 1.2 equiv. ^d mol product/mol catalyst. ^e mol product/(mol catalyst × time). ^f GC yield, based on aryl halide and product (2-methylnaphthalene as internal standard). ^g [Pd{2,6-(Pr₂PCH₂)₂-C₆H₃}{CO₂CF₃}] as catalyst. See reference 6(k). ^h Isomeric mixture (*E/Z* = 8/1).

For instance, the high-yielding reaction between methyl acrylate and iodobenzene proceeded with an average turnover frequency (TOF) of *ca.* 7400 h⁻¹ employing optimal conditions (entry 6). Of the polar solvents tested, in terms of average turnover frequency, *N*-methylpyrrolidone (NMP) was superior to *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) (entries 1, 4 and 5). Sodium carbonate was a more effective base than both sodium acetate and tributylamine (entries 1–3). Cyclometallated Pd(II) complexes frequently exhibit high thermal stability and all experiments were conducted at 140–160 °C; this could probably be extended to higher temperatures. In all cases investigated there was no noticeable formation of elemental palladium, and the final reaction mixture was always almost colourless or just faintly yellow. When the reaction was conducted with a lower aryl halide to catalyst ratio (below *ca.* 5 × 10⁴) the reaction can be performed in dry air without loss in efficiency. Only in cases where maximum TONs and average TOFs are desired should the purified aryl halides, olefins and solvents be used and the reaction conducted in an inert atmosphere.

Both the electronic nature of the olefin and steric hindrance are decisive factors for the efficiency of the catalyst; methyl acrylate for example gave a higher reaction rate and yield than did styrene or *n*-butyl acrylate when iodobenzene was employed (entries 7, 9 and 10). As expected, the reaction rate also depended on the nature of the aryl halide. Iodobenzene was more reactive than bromobenzene (entries 7 and 13), while complex **4** was incapable of converting aryl chloride to any extent.²¹ The dependence of the rate on both the nature of the olefin and the aryl halide, suggests that both the insertion of the olefin and the oxidative addition of aryl halide affect the overall rate.

In order to determine the fate of complex **4** in the catalytic experiments a ³¹P{¹H} NMR study of the reaction of iodobenzene with *n*-butyl acrylate using triphenylphosphine oxide as internal standard was carried out.²² Unfortunately, a detailed NMR monitoring of the species present was hampered by severe line broadening at the temperature at which complex **4** is catalytically active (approximately at 100 °C). After the completed reaction, however, no other peaks but the one ascribed to **5** (70.5 ppm, *vide supra*) along with the signal for the internal standard were present in the ³¹P{¹H} NMR spectrum, thus showing that a quantitative trifluoroacetate/iodide exchange had occurred. This quantitative conversion from **4** to **5** may be a result of a Pd(II)/Pd(IV) catalytic cycle based on oxidative addition of the aryl halide to the PCP complex. It should be noted that there are strong indications that Heck couplings catalysed by tridentate palladacycles proceed through Pd(II) and Pd(IV) rather than Pd(0) and Pd(II) intermediates due to

the high persistence of the bis-chelating ligand.²³ However, a thermally induced disassembly of the palladacyclic structure is also a possibility, although the aliphatic PCP complex **5** has far less built-in strain (a P–Pd–P angle of approximately 166°, *vide supra*) than previously reported aromatic PCP complexes used in the Heck reaction.^{6i,k}

It has been suggested by Milstein and co-workers that by changing the identity of the central donor atom in a PCP palladium complex from an sp² to an sp³ carbon the catalytic activity is increased.^{6k} In their study of the Heck reaction with the complexes [Pd{2,6-(Pr₂PCH₂)₂-C₆H₃}{CO₂CF₃}] (**I**) and [Pd{2,6-(Pr₂PCH₂)₂-3,5-(CH₃)₂-1-CH₂C₆H₃}{CO₂CF₃}] (**II**), **II** showed a substantially higher activity. However, these complexes differ not only with respect to the hybridisation of the central carbon donor atom, but also with respect to chelate ring size. An “sp³ effect” would be better demonstrated by comparing complex **4** with the analogous aromatic PCP complex **I**. From the reaction of iodobenzene with methyl acrylate, or *n*-butyl acrylate for that matter, it is clear that an increase in the rate of the reaction truly exists (Table 1, entry 7 *vs.* 8 and 10 *vs.* 11). The reactions in entries 7 and 10 are driven to the same yield or beyond with greater TONs and shorter reaction times than those reported in entries 8 and 11.²⁴ Thus, these results lend further support to the suggestion that a higher electron density on the metal centre, imparted by an sp³ carbon *versus* an sp² carbon, further increases the already high catalytic activity for a metallacyclic palladium phosphine complex in the Heck reaction.¹¹ Such a rate enhancing sp³ effect might also be observed in other catalytic reactions where aromatic metallacyclic bis-chelate complexes are employed as catalysts. This aspect is currently being investigated and will be reported in due course.

Experimental

General procedures and materials

All experiments with metal complexes and the phosphine ligand were carried out under an atmosphere of argon or nitrogen in a Braun glovebox equipped with an inert gas purifier or using standard Schlenk and high vacuum-line techniques. All non-deuterated solvents, reagent grade or better, were freshly distilled under a nitrogen atmosphere from sodium/benzophenone or CaH₂. All other commercially available reagents were purchased from Aldrich and used without purification. Compound **I** and lithium phosphide LiP^tBu₂ were prepared according to the literature.¹²

NMR spectra were recorded either on a Varian Unity 300 MHz instrument (¹H, ³¹P, ¹⁹F) or a Bruker ARX 500 MHz

spectrometer (^{13}C). $^{13}\text{C}\{^1\text{H}\}$ DEPT NMR spectroscopy was routinely recorded for each compound. The NMR spectroscopic measurements were performed in CDCl_3 unless otherwise stated. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane but were measured relative to the ^1H residual. ^{31}P NMR chemical shifts are reported in ppm downfield from an external 85% solution of phosphoric acid. ^{19}F NMR chemical shifts are reported in ppm downfield from an external sample of CClF_3 in CDCl_3 . 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 ^{13}C NMR spectra are reported according to Cohen and Sheppard.²⁵ Fast Atom Bombardment (FAB) mass spectroscopic data were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Gas chromatographic analyses were performed on a Varian 3300 instrument equipped with a 12-m BP-10 fused silica capillary column (0.22 ID). Elemental analyses were performed by MikroKemi AB, Uppsala, Sweden.

Except for the work-up of reaction mixtures, all Heck reactions were carried out under argon. Stock solutions of catalyst were used due to low concentrations and these were freshly prepared under inert conditions for each reaction and used only once. The solvents, aryl halides and bases were distilled when possible and used immediately. The olefin substrates were carefully deoxygenated by at least three freeze–pump–thaw cycles.

Typical procedure for the Heck reactions

The solvent (10 cm^3), aryl halide, base, olefin, 2-methylnaphthalene (internal standard) and a magnetic stirring bar were placed in a Schlenk tube with a screw cap. Three freeze–pump–thaw cycles were performed before addition of an appropriate volume of the catalyst stock solution. The Schlenk tube was sealed and placed in a pre-heated temperature-controlled oil-bath. The mixture was vigorously stirred for the desired time. A sample of 0.5 cm^3 was withdrawn from the reaction mixture, washed with 5% HCl (aq) and extracted with CH_2Cl_2 or diethyl ether as required for the GC determination of the yield. Work-up was achieved by pouring the cooled reaction mixture into an excess of 5% HCl (aq) and extracting with CH_2Cl_2 or Et_2O . The combined organic phases were neutralised with 10% NaHCO_3 (aq) and dried with MgSO_4 . After removal of the solvent the essentially pure products were analysed by ^1H NMR and MS. All of the products are known compounds.²⁶

Preparations

cis-1,3-Bis[(di-*tert*-butylphosphino)methyl]cyclohexane (2). A THF solution (10 cm^3) of **1** (2.20 g, 5.40 mmol) was carefully added to a cooled ($-60\text{ }^\circ\text{C}$) and stirred THF solution (15 cm^3) of LiP^tBu_2 (1.75 g, 10.8 mmol). The cooling bath was removed and the red solution was stirred overnight. The now yellow solution was quenched by 5 cm^3 of degassed water and the phases were separated. The water phase was further extracted with $3 \times 5\text{ cm}^3$ of diethyl ether and the combined organic phases were dried over silica. By decanting and removing the solvent under vacuum a colourless, highly viscous oil was isolated, which partly solidified upon standing. NMR spectroscopic analysis showed the product to be essentially pure and **2** was used without further purification. Yield 2.08 g (83%). ^1H NMR: δ 3.39 (m, 4H, CH_2P), 2.22–0.48 (m region, 14H, CH and CH_2), 1.11 (d, $^3J_{\text{PH}} = 1.2\text{ Hz}$, 18H, CH_3), 1.07 (d, $^3J_{\text{PH}} = 0.9\text{ Hz}$, 18H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 20.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 44.0 (t, $^3J_{\text{PC}} = 6.9\text{ Hz}$, CHCH_2CH), 38.2 (d, $^1J_{\text{PC}} = 20.4\text{ Hz}$, CH_2P), 34.8 (d, $^2J_{\text{PC}} = 9.4\text{ Hz}$, $(\text{CH})_2\text{CHCH}_2$), 31.2 (d, $^1J_{\text{PC}} = 7.4\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 31.0 (d, $^1J_{\text{PC}} = 7.2\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 29.8 (d, $^3J_{\text{PC}} = 27.9\text{ Hz}$, CHCH_2CH_2), 29.6 (d, $^2J_{\text{PC}} = 13.4\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 26.4 (s, $\text{CH}_2\text{CH}_2\text{CH}_2$).

cis-1,3-Bis[(di-*tert*-butylthiophosphoryl)methyl]cyclohexane (3). To a solution of compound **2** (437 mg, 1.09 mmol), dissolved in 10 cm^3 of toluene, S_8 was (1.12 g, 4.37 mmol) added and the mixture stirred overnight. Unreacted S_8 was removed by filtration and evaporation of the solvent from the filtrate gave a light yellow powder. The crude compound was loaded on a column of silica and trace amounts of sulfur were removed by eluting with *n*-hexane. The column was thereafter washed with CH_2Cl_2 to retrieve the product. Removal of the solvent and drying the white powder under vacuum gave **3** in an analytically pure state. Yield 426 mg (84%). ^1H NMR: δ 2.41 (m, 1H, CH_2), 2.13 (m, 2H, CH), 1.92 (m, 2H, CH_2), 1.70–1.37 (m region, 6H, CH_2P and CH_2), 1.30 (d, $^3J_{\text{PH}} = 4.2\text{ Hz}$, 18H, CH_3), 1.25 (d, $^3J_{\text{PH}} = 4.8\text{ Hz}$, 18H, CH_3), 0.88–0.74 (m region, 3H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 76.5 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 44.2 (t, $^3J_{\text{PC}} = 7.1\text{ Hz}$, CHCH_2CH), 37.9 (d, $^1J_{\text{PC}} = 17.5\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 37.4 (d, $^1J_{\text{PC}} = 17.6\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 35.2 (d, $^1J_{\text{PC}} = 5.4\text{ Hz}$, CH_2P), 34.0 (d, $^2J_{\text{PC}} = 3.4\text{ Hz}$, $(\text{CH})_2\text{CHCH}_2$), 28.1 (d, $^3J_{\text{PC}} = 28.1\text{ Hz}$, CHCH_2CH_2), 27.3 (bs, $\text{C}(\text{CH}_3)_3$), 25.9 (s, $\text{CH}_2\text{CH}_2\text{CH}_2$). MS (FAB⁺): $m/z = 464$ [$\text{C}_{24}\text{H}_{50}\text{P}_2\text{S}_2^+$]. $\text{C}_{24}\text{H}_{50}\text{P}_2\text{S}_2$ requires C, 62.0; H, 10.8; S, 13.8. Found: C, 61.6; H, 10.7; S, 14.1%.

[Pd(2)(CO₂CF₃)] (4). Phosphine **2** (22.3 mg, 55.7 μmol) and $[\text{Pd}(\text{CO}_2\text{CF}_3)_2]$ (18.5 mg, 55.7 μmol) were dissolved in 5 cm^3 of THF in a Schlenk tube. The tube was sealed, placed in an oil bath (80 $^\circ\text{C}$) and stirred for 1 h resulting in a colourless solution. The THF was removed under vacuum and the white precipitate dissolved in a minimum of boiling *n*-pentane. By storing the solution at $-18\text{ }^\circ\text{C}$ colourless needles were formed. Yield 31.4 mg (91%). ^1H NMR (CD_2Cl_2): δ 2.34–0.88 (m region, 13H, CH and CH_2), 1.36 (vt, $J_{\text{PH}} = 12.9\text{ Hz}$, 18H, CH_3), 1.32 (vt, $J_{\text{PH}} = 13.5\text{ Hz}$, 18H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 71.7 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 160.5 (m, C=O), 117.1 (q, $^1J_{\text{FC}} = 294\text{ Hz}$, CF_3), 60.1 (t, $^2J_{\text{PC}} = 2.9\text{ Hz}$, CHCHCH), 51.1 (vt, $J_{\text{PC}} = 15.0\text{ Hz}$, $(\text{CH})_2\text{CHCH}$), 35.5 (vt, $J_{\text{PC}} = 12.4\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 35.1 (vt, $J_{\text{PC}} = 26.2\text{ Hz}$, CH_2P), 34.7 (vt, $J_{\text{PC}} = 14.0\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 31.0 (vt, $J_{\text{PC}} = 17.4\text{ Hz}$, CHCH_2CH_2), 29.4 (vt, $J_{\text{PC}} = 6.0\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 29.0 (vt, $J_{\text{PC}} = 6.6\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 27.0 (s, $\text{CH}_2\text{CH}_2\text{CH}_2$). ^{19}F NMR (CD_2Cl_2): δ 50.6 (s). MS (FAB⁺): $m/z = 619$ [$\text{C}_{26}\text{H}_{49}\text{F}_3\text{O}_2\text{P}_2\text{Pd}^+$] (correct isotope pattern). $\text{C}_{26}\text{H}_{49}\text{F}_3\text{O}_2\text{P}_2\text{Pd}$ requires C, 50.4; H, 8.0. Found: C, 50.3; H, 8.0%.

[Pd(2)I] (5). To a solution of complex **4** (37.2 mg, 60.1 μmol) in 4 cm^3 of THF an excess of NaI (148 mg, 0.987 mmol) was added. The solution was vigorously stirred for 2 h at room temperature and the solvent was removed under vacuum. The resulting solid was washed repeatedly with CH_2Cl_2 . Removal of the solvent from the combined filtrates resulted in a white solid, which was dissolved in a minimum of boiling *n*-pentane. By storing the solution at $-18\text{ }^\circ\text{C}$ colourless cubic crystals were formed. Yield 35.3 mg (93%). ^1H NMR: δ 2.40–0.83 (m region, 13H, CH and CH_2), 1.45 (vt, $J_{\text{PH}} = 12.6\text{ Hz}$, 18H, CH_3), 1.43 (vt, $J_{\text{PH}} = 13.2\text{ Hz}$, 18H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 70.5 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 72.3 (t, $^2J_{\text{PC}} = 5.2\text{ Hz}$, CHCHCH), 50.4 (vt, $J_{\text{PC}} = 14.2\text{ Hz}$, $(\text{CH})_2\text{CHCH}$), 36.1 (vt, $J_{\text{PC}} = 13.0\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 35.6 (vt, $J_{\text{PC}} = 14.8\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 34.5 (vt, $J_{\text{PC}} = 26.6\text{ Hz}$, CH_2P), 33.0 (vt, $J_{\text{PC}} = 16.4\text{ Hz}$, CHCH_2CH_2), 30.7 (vt, $J_{\text{PC}} = 5.6\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 29.7 (vt, $J_{\text{PC}} = 5.6\text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 26.4 (s, $\text{CH}_2\text{CH}_2\text{CH}_2$). MS (FAB⁺): $m/z = 632$ [$\text{C}_{24}\text{H}_{49}\text{IP}_2\text{Pd}^+$] (correct isotope pattern). $\text{C}_{24}\text{H}_{49}\text{IP}_2\text{Pd}$ requires C, 45.5; H, 7.8. Found: C, 45.5; H, 7.6%.

Crystallography

Intensity data were collected with a Bruker Smart CCD system.²⁷ The intensity was corrected for Lorentz, polarization and absorption effects using SADABS.²⁸ The first 50 frames were collected again at the end to check for decay and none was observed. All reflections were merged and integrated using SAINT.²⁹ The structure was solved by direct methods and

refined by full matrix least-squares calculations on F^2 using SHELXTL5.1.³⁰ Non-H atoms were refined with anisotropic displacement parameters. The hydrogen atoms on methine and methylene carbons were constrained to parent sites, using a riding model. Methyl hydrogens were not included in the calculation.

Crystal data. $C_{24}H_{49}IP_2Pd$, $M = 632.87$, monoclinic, $a = 12.102(2)$, $b = 15.035(3)$, $c = 15.875(3)$ Å, $\beta = 100.27(3)^\circ$, $V = 2842.3(10)$ Å³, $T = 293$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.860$ mm⁻¹, 29034 reflections measured, 8936 unique ($R_{\text{int}} = 0.0692$) which were used in all calculations. The final $wR(F^2)$ was 0.1303 (all data). The $R(F)$ was 0.0448 ($I > 2\sigma(I)$).

CCDC reference number 177302.

See <http://www.rsc.org/suppdata/dt/b1/b111487p/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank Mr Daniel Olsson for helpful assistance in the laboratory. Financial support by the TFR (The Swedish Research Council for Engineering Sciences) and the NFR (The Swedish Natural Science Research Council) is gratefully acknowledged.

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- Using the reaction condition in Table 1, entry 1 with complex **5** as precatalyst results in the same reaction rate within experimental errors.
- Addition of molten salts to promote the reaction was never considered, since nothing is gained by using such an expensive reagent.
- 2.4 mmol **4**, 1.6 mmol PhI, 0.2 g Na₂CO₃, 3.2×10^{-3} mmol of **4**, 3.2×10^{-3} mmol of P(O)Ph₃ were dissolved in 0.5 cm³ of NMP inside a J. Young NMR tube. The reaction was monitored at 120 ± 5 °C until completion of the catalytic reaction (TON = 500).
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