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# 2-(1-(Dimethylamino)ethyl)phenylpalladium(II) complexes 5-functionalized with fluorous silyl tails

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Dedicated to Prof. Brian James, University of British Columbia, Vancouver, BC, Canada on the occasion of his 70th birthday.

**Abstract**

New fluorous-organometallics based on the chiral ligand α-methyl-*N*,*N*-dimethylbenzylamine (TMBA) were prepared by treatment of fluorous silyl bromide reagents with in situ 4-lithiated TMBA to give fluorous *N*,*N*-dimethyl(α-methyl-4-trialkylsilylbenzyl)amine ligands **1a**–**1c** that vary in the number of fluorous tails attached to the Si atom. Ligands **1a**–**1c** were successfully cyclo-palladated by treatment with $Pd(OAc)_2$/LiCl in methanol to furnish the corresponding chloride-bridged dimeric arylpalladium(II) complexes **2a**–**2c** in good yields. The latter derivatives could be converted into monomeric Lewis-base adducts by complexation with pyridine (**3a**–**3c**), or triphenylphosphine (**4a**–**4c**). The crystal structure of triphenylphosphine complex **4a** has been elucidated. To probe their fluorophilicity, the partition coefficient of each of the derivatives in the fluorous biphasic solvent (FBS) system perfluoromethylcyclohexane/*n*-octane has been determined.
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*Keywords:* Fluorous biphasic separation; Fluorophilicity; *C*,*N*-Chelating ligand, Pd(II); α-Methyl-*N*,*N*-dimethylbenzylamine; Cyclo-metallation; Partition coefficient; FBS

## 1. Introduction

Separation of spent catalysts (or residues) from product/substrate streams still represents one of the largest challenges in homogeneous catalysis. Over the past years, several approaches have been successfully introduced in this field. Suitable enlargement of transition metal catalysts by attachment to soluble carrier molecules such as dendrimers and hyper-branched polymers has been studied in detail [1]. This has facilitated separation and reuse of the nano-scale catalytic entities by means of ultra-filtration and several promising approaches for continuous applications have been recently communicated [2]. Another method of separation is provided by aqueous biphasic systems involving the introduction of sulfonato or other groups onto the catalyst to increase its solubility in water [3]. After the reaction has completed, the catalyst can be easily recovered by phase separation. Although these methods have been applied successfully in several cases, mass transfer limitation issues,[2] incompatibility with water or labor-intensive synthetic requirements have limited their broader application.

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[2] This is largely due to the rather insoluble character of many organic molecules in aqueous media.

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Fluorous biphasic separation [4] is a rather recent approach to solve the issue of homogenous catalyst separation. Following pioneering work by Horváth and Rábai [5], numerous perfluoroalkyl-functionalized metal complexes have emerged which were successfully applied in a number of interesting catalytic transformations [6–8]. The technique takes advantage of the preferential solubility of fluorous complexes in perfluorocarbon solvents that have temperature dependant miscibility with regular organic solvents. By cooling the reaction mixture below its consolute temperature, phase separation can be induced allowing biphasic separation to proceed while the catalytic reaction itself can take place under truly homogeneous conditions above the consolute temperature. This unique feature of fluorous biphasic solvent (FBS) mixtures removes any liquid–liquid mass transfer limitations that are often associated with aqueous–organic biphasic systems. Another clear advantage is the general inertness of perfluorocarbon solvents, which render them especially suitable as solvent for reactive homogeneous catalysts that are often not compatible with aqueous conditions.

A class of well-studied FBS-type catalysts are based on (non-chiral) coordination complexes derived from phosphine and/or phosphite ligands [6–8]. Although these complexes have been employed successfully in hydrogenation, hydrosilylation, hydroformylation and methoxycarbonylation processes, through dissociation of the metal to phosphorus bond the metal center in these complexes is potentially subject to leaching under long-term exposure to the process conditions [8]. Complexes with relatively stable σ-bonded metal centers, in particular those that are bonded through a M–C σ-bond, could provide an increased stability with respect to metal leaching. The increased thermal stability under the process conditions is especially relevant in the case of asymmetric catalysts that derive their chirality from a chiral ligand backbone. In this work we report on the synthesis and characterization of such systems which are based on the chiral *N*,*N*-dimethyl-α-methylbenzylamine ligand. The influence of the degree of perfluoroalkylation of this ligand on its physical properties will be discussed.

## 2. Experimental

### 2.1. General procedures and instrumentation

Air-sensitive manipulations were carried out in an inert dinitrogen atmosphere. Solvents were carefully dried and distilled prior to use. The perfluoroalkyl chloride/bromide reagents $F_{13}C_6CH_2CH_2Si(CH_3)_2Cl$, $(F_{17}C_8CH_2CH_2)_2Si(CH_3)Br$ and $(F_{17}C_8CH_2CH_2)_3SiBr$ were prepared according to literature procedures [9]. All NMR experiments were obtained using a Varian Inova 200 or 300 MHz spectrometer with TMS as an external standard. Chemical shifts ($\delta$) are reported in ppm. Combustion analyses were outsourced to Dornis und Kolbe, Microanalytisch Laboratorium, Müllheim a/d Ruhr, Germany. MALDI-TOF-MS spectrometric measurements were acquired using a Voyager-DE BioSpectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA, USA) mass spectrometer and 3,5-dihydroxybenzoic acid (for the ligands) or 9-nitroanthracene (for the Pd(II) complexes) were used as matrices. Reported MALDI-TOF-MS mass values are not calibrated. Reported melting points were measured in open capillaries and are uncorrected.

### 2.2. Syntheses

#### 2.2.1. Syntheses of **1a–1c**

Commercially available 4-bromo-α-methyl-*N*,*N*-dimethylbenzylamine (4-Br-TMBA, *ee* 98.9% *R*) was used as a starting point for the attachment of perfluoroalkyl chains onto the ligand structure. To a stirred solution of 4-bromo-α-methylbenzyl-*N*,*N*-dimethylamine (3 mmol) in $Et_2O$ (30 mL) cooled to −78 °C, was added a solution of *t*-BuLi (6 mmol) in pentane. The reaction mixture was stirred for 3 h at −80 °C, after which 3 mmol of the appropriate silyl-bromide or -chloride was added. The cooling bath was removed and the mixture stirred for 18 h, where after it was poured into an aqueous $NH_4Cl$ solution and extracted with pentane (2 × 25 mL). After drying of the combined organic layers with $Na_2SO_4$, the products were isolated by thorough evaporation of the solvents.

(**1a**) Yield after distillation: 56%; b.p.: 125–135 °C/0.6 mm Hg; $n_D^{21} = 1.4163$; $[\alpha]_D^{20} = +22.12°$ ($c = 7.66$ M, *n*-hexane); $C_{20}F_{13}H_{24}NSi$ requires: C, 43.40; H, 4.37; N, 2.53. Found: C, 42.41; H, 4.10; N, 2.74%. GC–MS (EI): *m*/*z* 553 ($M^+$), (calc. 553.2). $^1$H NMR ($CDCl_3$): $\delta$ 7.45 (d, $^3J = 8.0$ Hz, 2H ArH), 7.32 (d, $^3J = 8.0$ Hz, 2H ArH), 3.25 (q, $^3J = 7.7$ Hz, 1H, C*H*N), 2.21 (s, 6H, N(C$H_3$)$_2$), 2.20–1.90 (m, 2H, FC-C$H_2$), 1.38 (d, $^3J = 7.7$ Hz, 2H, NCHC$H_3$); 1.02–0.96 (m, 2H, SiC$H_2$), 0.33 (s, 6H, Si(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 145.5, 135.5, 133.4, 127.2 (Ar*C*), 65.9 (*C*HN); 43.2 (N(*C*H$_3$)$_2$), 25.9 (t, $^2J$(F–C) = 24.0 Hz, $CF_2CH_2$), 20.0 (NCH*C*H$_3$), 5.2 (Si*C*H$_2$), −3.5 (Si*C*H$_3$).

(**1b**) This compound was used without further purification. Yield: 90%. $[\alpha]_D^{20} = +14.0°$ ($c = 1.23$ M, *n*-hexane). $C_{31}F_{34}H_{25}NSi$ requires: C, 34.30; H, 2.32; N, 1.29; Si, 2.59. Found: C, 34.22; H, 2.38; N, 1.26; Si, 2.66%. MALDI-TOF-MS (3,5-dihydroxybenzoic acid): *m*/*z* 1091.7 $(M + H)^+$ (calc. 1086.6). $^1$H NMR ($C_6D_6$): $\delta$ 7.32 (d, $^3J = 8.0$ Hz, 2H, ArH), 7.20 (d, $^3J = 8.0$ Hz, 2H, ArH), 3.08 (q, $^3J = 7.7$ Hz, 1H, C*H*N), 2.04 (s, 6H, N(C$H_3$)$_2$), 2.00–1.80 (m, 4H, FC-C$H_2$), 1.20 (d, 3H, $^3J = 7.7$ Hz, NCHC$H_3$), 0.92–0.75 (m, 4H, SiC$H_2$), −0.06 (s, 3H, SiC$H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 147.8, 133.6, 132.2, 127.7 (Ar*C*), 65.9 (*C*HN), 42.9 (N(*C*H$_3$)$_2$), 26.0 (t, $^2J$(F–C) = 25 Hz, $CF_2CH_2$), 20.0 (NCH*C*H$_3$), 3.5 (Si*C*H$_2$), −6.6 (Si*C*H$_3$).

(**1c**) This compound was used without further purification. Yield: 96%. $[\alpha]_D^{20} = +8.2°$ ($c = 0.50$ M, *n*-hexane). $C_{40}F_{51}H_{26}NSi$ requires: C, 31.66; H, 1.73; N, 0.92; Si, 1.85. Found: C, 31.69; H, 1.67; N, 0.99; Si, 1.87%.

MALDI-TOF-MS (3,5-dihydroxybenzoic acid): *m/z* 1521.1 $(M + H)^+$ (calc. 1518.1). $^1$H NMR ($C_6D_6/C_6F_6$, 50 °C): $\delta$ 7.33 (d, $^3J = 7.9$ Hz, 2H, ArH), 7.19 (d, $^3J = 7.9$ Hz, 2H, ArH), 3.08 (q, $^3J = 6.7$ Hz, 1H, C*H*N), 2.07 (s, 6H, N(C$H_3$)$_2$), 2.09–1.87 (m, 6H, $CF_2CH_2$), 1.21 (d, $^3J = 6.7$ Hz, 3H, NCHC$H_3$), 0.97–0.83 (m, 6H, SiC$H_2$). $^{13}$C{$^1$H} NMR ($C_6D_6/C_6F_6$, 50 °C): $\delta$ 148.4, 133.6, 129.4, 127.9 (ArC), 65.8 (*C*HN), 42.6 (N(*C*H$_3$)$_2$), 25.7 (t, $^2J$(F–C) = 25 Hz, FC-*C*H$_2$), 19.5 (NCH*C*H$_3$), 1.4 (Si*C*H$_2$).

### 2.2.2. Syntheses of **2a**

(**2a**) Ligand **1a** (1 mmol) was added to a mixture of $Pd(OAc)_2$ (1 mmol) in MeOH (10 mL). The resulting solution was stirred for 1 h, after which a solution of LiCl (0.15 g) in MeOH (10 mL) was added. After 1 h, $CH_2Cl_2$ (50 mL) was added and the mixture was subsequently washed with water (100 mL). The organic layer was dried over $Na_2SO_4$, than filtered and the filtrate concentrated in vacuo. The residue was obtained as a yellow solid and was further purified by crystallization from warm MeOH. The compound (90% yield) exists in solution as a 1:1 mixture of *cis*- and *trans*-isomers; m.p.: 141 °C. $C_{20}ClF_{13}H_{24}NPdSi$ requires: C, 34.60; H, 3.34; N, 2.02; Si, 4.05. Found: C, 34.70; H, 3.33; N, 1.94; Si, 4.13%. MALDI-TOF-MS (9-nitro-anthracene): *m/z* 1355.8 $(2M - Cl)^+$ (calc. 1353.2), 2049.6 $(3M - Cl)^+$ (calc. 2047.6). $^1$H NMR ($CDCl_3$): $\delta$ 7.39 (s, 1H, ArH, one isomer), 7.31 (s, 1H, ArH, other isomer), 7.08 (d, $^3J = 7.4$ Hz, 1H, ArH); 6.78 (d, $^3J = 7.4$ Hz, 1H, ArH), 3.87 (m, 1H, C*H*CH$_3$), 2.91 (s, 3H, NC$H_3$), 2.65 (s, 3H, NC$H_3$), 2.08–1.81 (m, 2H, C$H_2$CF$_2$), 1.60–1.49 (m, 3H, CHC$H_3$), 0.99–0.88 (m, 2H, C$H_2$Si), 0.27 (s, 6H, SiC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 153.8, 153.6, 143.8, 143.7, 138.4, 138.0, 135.1, 134.9, 130.0, 122.1 (Ar*C* both isomers), 75.4 (*C*HCH$_3$, one signal overlapping), 52.7, 52.4, 47.4, 47.0 (NCH$_3$ both isomers), 26.2 (t, $^2J$(F–C) = 25.0 Hz, *C*H$_2$CF$_2$), 18.9 and 18.5 (CH*C*H$_3$ both isomers), 5.4 (*C*H$_2$Si), −2.9, −3.4 (Si*C*H$_3$ both isomers).

### 2.2.3. Syntheses of **2b**

To a mixture of $Pd(OAc)_2$ (0.46 mmol) in FC 72 (10 mL) was added **1b** (0.46 mmol), followed by the addition of 2 mL of EtOH. The biphasic system was stirred for 18 h, followed by the addition of LiCl (0.15 g) dissolved in EtOH (3 mL). Stirring was continued for another 1 h. The resulting mixture was poured into water and $CH_2Cl_2$ (20 mL) was added. The organic layer was separated and the aqueous layer was extracted with FC-72 (10 mL). The combined organic layers were dried over $Na_2SO_4$ and the filtered solution was concentrated in vacuo to furnish the product as a brown oil. Yield: 98%. The compound exists in solution as a 1:1 mixture of *cis*- and *trans*-isomers. $C_{31}ClF_{34}H_{24}NPdSi$ requires: C, 30.36; H, 1.97; N, 1.14; Si, 2.29. Found: C, 30.15; H, 1.86; N, 0.97; Si, 2.35%. MALDI-TOF-MS (9-nitro-anthracene): *m/z* 2421.13 $(2M - Cl)^+$ (calc. 2419.0). $^1$H NMR ($CDCl_3$): $\delta$ 7.35 (s, 1H, ArH, one isomer), 7.31 (s, 1H, ArH, other isomer), 7.05 (d, $^3J = 7.0$ Hz, 1H, ArH), 6.81 (d, $^3J = 7.0$ Hz, 1H, ArH), 4.00–3.91 (bq, $^3J = 5.8$ Hz, 1H, C*H*CH$_3$), 2.91 (bs, 3H, NC$H_3$), 2.65 (bs, 3H, NC$H_3$), 2.10–1.81 (m, 4H, C$H_2$CF$_2$), 1.58 (d, $^3J = 5.8$ Hz, 3H, CHC$H_3$), 1.03–0.88 (m, 4H, C$H_2$Si), 0.32 (s, 3H, SiC$H_3$). $^{13}$C{1H} NMR ($CDCl_3$): $\delta$ 154.5, 154.3, 144.1, 144.0, 138.4, 138.1, 131.7, 130.1, 122.4 (Ar*C* both isomers), 77.4, 75.5 (*C*HCH$_3$ both isomers), 52.4, 47.2 (NCH$_3$ both isomers, overlapping signals), 26.0 (t, $^2J$(F–C) = 24.2 Hz, *C*H$_2$CF$_2$), 18.6, 18.3 (CH*C*H$_3$ both isomers), 3.7 (*C*H$_2$Si), −5.6 (Si*C*H$_3$).

### 2.2.4. Syntheses of **2c**

The product was prepared analogously to **2b** and was isolated as a brown oil. Yield: 99%. Only one isomer was observed in the NMR spectra, presumably the *trans* dimer (see text). $C_{40}ClF_{51}H_{25}NPdSi$ requires: C, 28.97; H, 1.52; N, 0.84; Si, 1.69. Found: C, 28.69; H, 1.48; N, 0.79; Si, 1.77%. MALDI-TOF-MS (9-nitro-anthracene): *m/z* 3282.4 $(2M - Cl)^+$ (calc. 3283.0). $^1$H NMR ($CDCl_3/C_6F_6$, 60 °C): $\delta$ 7.36 (s, 1H, ArH), 7.09 (d, $^3J = 7.2$ Hz, 1H, ArH), 6.90 (d, $^3J = 7.2$ Hz, 1H, ArH), 3.94 (bq, $^3J = 6.0$ Hz, 1H, C*H*CH$_3$), 2.95 (s, 3H, NC$H_3$), 2.69 (s, 3H, NC$H_3$), 2.19–1.90 (m, 4H, C$H_2$CF$_2$), 1.64 (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 1.90–1.11 (m, 4H, C$H_2$Si). $^{13}$C{$^1$H} NMR ($CDCl_3/C_6F_6$, 60 °C): $\delta$ 155.1, 144.4, 136.9, 130.1, 128.8, 122.5 (Ar*C*), 75.5 (*C*HCH$_3$), 52.2, 46.8 (NCH$_3$), 26.0 (t, $^2J$(F–C) = 23.2 Hz, *C*H$_2$CF$_2$), 17.9 (CH*C*H$_3$), 2.0 (*C*H$_2$Si).

### 2.2.5. Synthesis of pyridine complexes **3a–3c**

To a solution of the palladium compounds **2a**, **2b** or **2c** (1 mmol) in $CH_2Cl_2$ (20 mL) was added pyridine (1.2 mmol). The reaction mixture was stirred for 1 h after which all volatiles were carefully removed in vacuo. The pyridine complexes **3a** and **3b** were obtained as yellow solids in quantitative yield. Complex **3c** was obtained as a yellow oil. Product **3a** was crystallized from hot EtOH; m.p.: 123 °C. $C_{25}ClF_{13}H_{28}N_2PdSi$ requires: C, 38.82; H, 3.65; N, 3.62; Si, 3.63. Found: C, 38.94; H, 3.70; N, 3.55; Si 3.60%. $^1$H NMR ($CDCl_3$): $\delta$ 8.90 (d, $^3J = 4.8$ Hz, 2H, Pyr$H_{ortho}$), 7.85 (t, $^3J = 7.7$ Hz, 1H, Pyr$H_{para}$), 7.39–7.34 (m, 2H, Pyr$H_{meta}$); 7.09 (d, $^3J = 7.0$ Hz, 1H, ArH), 6.90 (d, $^3J = 7.0$ Hz, 1H, ArH), 6.03 (s, 1H, ArH), 3.86 (q, $^3J = 6.6$ Hz, 1H, C*H*CH$_3$), 2.98 (s, 3H, NC$H_3$), 2.76 (s, 3H, NC$H_3$), 1.94–1.78 (m, 2H, C$H_2$CF$_2$), 1.62 (d, $^3J = 6.6$ Hz, 3H, CHC$H_3$), 0.75–0.69 (m, 2H, C$H_2$Si), 0.07 (s, 6H, SiC$H_3$). $^{13}$C{1H} NMR ($CDCl_3$): $\delta$ 154.5, 153.9, 149.2, 138.0, 137.2, 134.6, 129.8, 125.2, 122.0 (ArC + PyrC), 76.1 (*C*HCH$_3$), 52.5, 47.7 (NCH$_3$), 26.0 (t, $^2J$(F–C) = 24.2 Hz, *C*H$_2$CF$_2$), 19.4 (CH*C*H$_3$), 5.2 (*C*H$_2$Si), −3.30 (Si*C*H$_3$).

Product (**3b**) was crystallized from benzene; m.p.: 128 °C. $C_{36}ClF_{34}H_{29}N_2PdSi$ requires: C, 33.12; H, 2.24; N, 2.15; Si, 2.15. Found: C, 32.96; H, 2.15; N, 2.06; Si, 2.33%. $^1$H NMR ($CDCl_3$): $\delta$ 8.89 (d, $^3J = 4.8$ Hz, 2H, Pyr$H_{ortho}$), 7.82 (t, $^3J = 7.7$ Hz, 1H, Pyr$H_{para}$), 7.39-7.28 (m, 2H, Pyr$H_{meta}$), 7.07 (d, $^3J = 7.0$ Hz, 1H, ArH), 6.93 (d,

$^3J = 7.0$ Hz, 1H, ArH), 6.01 (s, 1H, ArH), 3.88 (q, $^3J = 6.6$ Hz, 1H, C*H*CH$_3$), 2.99 (s, 3H, NC*H*$_3$), 2.78 (s, 3H, NC*H*$_3$), 2.00–1.71 (m, 4H, C*H*$_2$CF$_2$), 1.64 (d, $^3J = 6.6$ Hz, 3H, CHC*H*$_3$), 0.99–0.77 (m, 4H, C*H*$_2$Si), 0.13 (s, 3H, SiC*H*$_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 155.3, 153.8, 149.6, 138.1, 137.2, 131.4, 130.0, 125.3, 122.3 (ArC + PyrC), 76.1 (*C*HCH$_3$), 52.5, 47.7 (N*C*H$_3$), 25.8 (t, $^2J$(F–C) = 23.6 Hz, *C*H$_2$CF$_2$), 19.4 (CH*C*H$_3$), 3.4 (*C*H$_2$Si), −5.8 Si(*C*H$_3$).

Black oily **3c** (yield of crude **3c** was 99%) was extracted with $CH_2Cl_2$ (20 mL), then filtered through Celite and the filtrate concentrated in vacuo. Fluorous **3c** was isolated as a yellow oil. Yield 76%. $C_{45}ClF_{51}H_{30}N_2PdSi$ requires: C, 31.11; H, 1.74; N, 1.61; Si, 1.62. Found: C, 31.06; H, 1.71; N, 1.56; Si, 1.64%. $^1$H NMR ($CDCl_3$): $\delta$ 8.88 (d, $^3J = 4.8$ Hz, 2H, PyrH$_{ortho}$), 7.82 (t, $^3J = 7.7$ Hz, 1H, PyrH$_{para}$), 7.39-7.28 (m, 2H, PyrH$_{meta}$), 7.03 (d, $^3J = 7.0$ Hz, 1H, ArH), 6.96 (d, $^3J = 7.0$ Hz, 1H, ArH), 6.00 (s, 1H, ArH), 3.88 (q, $^3J = 6.4$ Hz, 1H, C*H*CH$_3$), 2.98 (s, 3H, NC*H*$_3$), 2.77 (s, 3H, NC*H*$_3$), 2.14–1.63 (m, 6H, C*H*$_2$CF$_2$), 1.65 (d, $^3J = 6.4$ Hz, 3H, CHC*H*$_3$), 1.00–0.79 (m, 6H, C*H*$_2$Si). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 156.0, 153.7, 149.6, 150.0, 138.0, 137.3, 130.0, 128.4 125.3, 122.3 (ArC + PyrC), 76.2 (*C*HCH$_3$), 52.5, 47.7 (N*C*H$_3$), 25.6 (t, $^2J$(F–C) = 23.0 Hz, *C*H$_2$CF$_2$), 19.3 (CH*C*H$_3$), 1.5 (*C*H$_2$Si).

### 2.2.6. Synthesis of triphenylphosphine complexes *4a–4c*

To a solution of complexes **2a**, **2b** or **2c** (1 mmol) in $CHCl_3$ (20 mL) was added $PPh_3$ (1 mmol). The reaction mixture was stirred for 1 h, after which the solvent was removed in vacuo. The products were isolated quantitatively as waxy oils, but could be crystallized from either hot EtOH (**4a**) or $Et_2O$ (**4b**). Compound **4c** was isolated as a dark brown oil and was purified by extracting a solution of **4c** in FC-72 with benzene: the dark material concentrated into the benzene layer while a clear, light yellow-colored FC-72-solution (of **4c**) remained. Finally **4c** was isolated as a light yellow-colored oil.

Complex (**4a**): m.p.: 125 °C, $C_{38}ClF_{13}H_{48}NPdPSi$ requires: C, 47.21; H, 5.00; N, 1.45; Si, 2.91; P, 3.20. Found: C, 47.27; H, 4.85; N, 1.30; Si, 2.96; P, 3.31%. $^1$H NMR ($CDCl_3$): $\delta$ 7.78–7.72 (m, 6H, aromatic *H*, P-ArH$_{ortho}$), 7.44–7.28 (m, 9H, P-ArH), 6.99 (d, $^3J = 7.3$ Hz, 1H, ArH), 6.95 (d, 1H, $^3J = 7.3$ Hz, ArH), 6.61 (d, 1H, $^4J$(P–H) = 7.3 Hz, ArH), 3.85–3.81 (m, *J* unresolved, 1H, C*H*CH$_3$), 2.88 (s, 3H, NC*H*$_3$), 2.80(s, 1H, NC*H*$_3$), 1.79 (d, $^3J = 5.7$ Hz, 3H, CHC*H*$_3$), 1.71–1.62 (m, 2H, C*H*$_2$CF$_2$), 0.44–0.39 (m, 2H, C*H*$_2$Si), −0.23 (s, 3H, SiC*H*$_3$), −0.22 (d, $J = 3.0$ Hz, 3H, SiC*H*$_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 156.0, 150.3, 143.9, 135.5, 135.3, 133.7, 132.4, 130.7, 129.2, 128.3, 128.2, 122.4 (ArC + P-ArC), 75.5 (*C*HCH$_3$), 50.7, 46.8 (N*C*H$_3$), 26.0 (t, $^2J$(F–C) = 34.3 Hz, *C*H$_2$CF$_2$), 21.9 (CH*C*H$_3$), 5.2 (*C*H$_2$Si), −3.6, −3.7 (d, $J = 4.8$ Hz, SiC*H*$_3$); $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 43.7 ($PPh_3$).

Complex (**4b**): m.p.: 62 °C. $C_{49}ClF_{34}H_{39}NPdPSi$ requires: C, 39.53; H, 2.64; N, 0.94; Si, 1.89. Found: C, 39.41; H, 2.60; N, 1.04; Si, 1.96%. $^1$H NMR ($CDCl_3$): $\delta$ 7.78–7.71 (m, 6H, P-ArH$_{ortho}$), 7.44–7.28 (m, 9H, P-ArH), 7.01 (d, $^3J = 7.2$ Hz, 1H, ArH), 6.92 (d, $^3J = 7.3$ Hz, 1H, ArH), 6.57 (d, $^4J$(P–H) = 6.1 Hz, ArH), 3.85–3.81 (m, *J* not resolved, 1H, C*H*CH$_3$), 2.88 (s, 3H, NC*H*$_3$), 2.80 (s, 1H, NC*H*$_3$), 1.80 (d, $^3J = 6.4$ Hz, 3H, CHC*H*$_3$), 1.74–1.60 (m, 4H, C*H*$_2$CF$_2$), 0.53–0.46 (m, 4H, C*H*$_2$Si), −0.22 (s, 6H, SiC*H*$_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 156.8, 150.8, 144.0, 135.5, 135.4, 132.1, 131.5, 130.9, 129.3, 128.3, 128.2, 122.6 (ArC + P-ArC), 75.5 (*C*HCH$_3$), 50.6, 46.8 (N*C*H$_3$), 25.7 (t, $^2J$(F–C) = 22.4 Hz, *C*H$_2$CF$_2$), 21.7 (CH*C*H$_3$), 3.2 (*C*H$_2$Si), −6.2 (Si*C*H$_3$); $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 43.9 ($PPh_3$).

Complex (**4c**): Light, yellow-colored oil, yield 58%. $C_{58}ClF_{51}H_{40}NPdPSi$ requires: C, 36.27; H, 2.10; N, 0.73; Si, 1.46; P, 1.61. Found: C, 36.18; H, 2.02; N, 0.78; Si, 1.42; P, 1.56%. $^1$H NMR ($CDCl_3$): $\delta$ 7.77–7.68 (m, 6H, P-ArH$_{ortho}$), 7.34–7.26 (m, 9H, P-ArH), 7.04 (d, $^3J = 7.3$ Hz, 1H, ArH), 6.88 (d, $^3J = 7.3$ Hz, 1H, ArH), 6.52 (d, $^4J$(P–H) = 6.5 Hz, 1H, ArH), 3.85–3.47 (m, *J* not resolved, 1H, C*H*CH$_3$), 2.86 (s, 3H, NC*H*$_3$), 2.80 (s, 1H, NC*H*$_3$), 1.80 (d, $^3J = 6.2$ Hz, 3H, CHC*H*$_3$), 1.79–1.59 (m, 6H, C*H*$_2$CF$_2$), 0.85–0.49 (m, 6H, C*H*$_2$Si). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 157.2, 151.3, 144.1, 135.6, 135.4, 133.4, 132.4, 132.3, 132.2, 132.0, 131.3, 131.0, 129.3, 128.8, 128.7, 128.2, 123.0 (ArC + P-ArC), 75.5 (*C*HCH$_3$), 50.6, 46.8 (N*C*H$_3$), 25.4 (t, $^2J$(F–C) = 24.9 Hz, *C*H$_2$CF$_2$), 21.5 (CH*C*H$_3$), 1.0 (*C*H$_2$Si). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 44.3 ($PPh_3$).

### 2.3. X-ray crystal structure determination of *4a*

$C_{38}H_{38}ClF_{13}NPPdSi$, $F_w = 956.60$, yellow block, $0.18 \times 0.09 \times 0.06$ mm$^3$, monoclinic, $P2_1$ (no. 4), $a = 10.5589(3)$ Å, $b = 8.1123(3)$ Å, $c = 23.3392(7)$ Å, $\beta = 91.632(1)°$, $V = 1998.35(11)$ Å$^3$, $Z = 2$, $D_{calc} = 1.590$ g/cm$^3$, $\mu = 0.691$ mm$^{-1}$. 18 626 reflections were measured at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å$^{-1}$ on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda = 0.71073$ Å). An absorption correction was not considered necessary. The crystal appeared to be cracked into two fragments. This was taken into account during the intensity evaluation and in the merging process, resulting in 8994 unique reflections. The structure was solved with automated Patterson Methods [10] and refined with SHELXL-97 [11] on $F^2$ of all reflections as a HKLF5 refinement. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. The flourous tail was disordered over two conformations. 628 parameters were refined with 593 restraints. $R_1/wR_2$ [$I > 2\sigma(I)$]: 0.0352/0.0631. $R_1/wR_2$[all refl.]: 0.0481/0.0673. $S = 1.060$. Flack parameter [12] $x = -0.01(3)$. Residual electron density between −0.52 and 0.51 e/Å$^3$. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package [13].

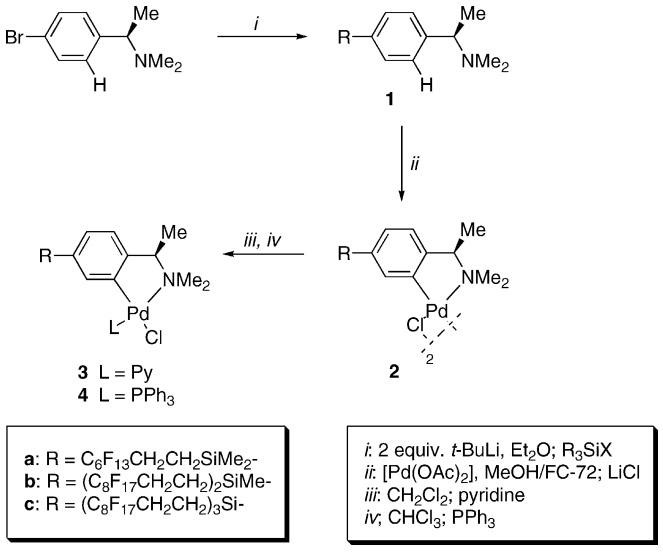
### 2.4. Determination of partition coefficients

A known amount of fluorous compound (between 1 and 15 μmol) was dissolved in PFMCH (2.0 mL) and octane (2.0 mL). The two layers were warmed up to 50 °C until a clear, single phase solution was obtained. Then the system was equilibrated at 0 °C for 30 min. When two separated layers were obtained, an aliquot (500 μL) from each layer was taken by syringe and the amount of palladium determined by ICP-AAS analysis. Alternatively, all solvent was evaporated and the weight of the residue obtained from each phase was determined. The partition coefficients ($P$) were calculated by dividing the amount of material found in the fluorous phase by the amount found in the organic phase [8e].

## 3. Results and discussion

### 3.1. Syntheses and analyses of the fluorous alkylsilyl-substituted ligands

The preparation of **1a**–**1c** (Scheme 1) was achieved by reacting in situ prepared aryllithium **1**-Li, which was generated by a bromine–lithium exchange reaction in $Et_2O$/hexane at −78 °C, with the appropriate silyl chloride or bromide reagent $C_6F_{13}CH_2CH_2Si(Me)_2Cl$, $(C_8F_{17}CH_2CH_2)_2Si(Me)Br$ or $(C_8F_{17}CH_2CH_2)_3SiCl$, respectively [9]. Compounds **1a**–**1c** were isolated in good yields (56–96%) as turbid oils and their structural formulations were supported by NMR-, MS-data and elemental analyses. In particular, the presence of the fluorous tails was easily monitored in the $^1H$ NMR spectra by the appearance of new signals corresponding to the $-(CH_2CH_2)_{3-n}SiMe_n-$ fragments ($n = 0$–2) of the perfluoroalkyl chain. Upon the introduction of an increasing amount of perfluoroalkyl tails, the solubility properties of these fluorous compounds changed dramatically: whereas **1a** is highly soluble in




Scheme 1.

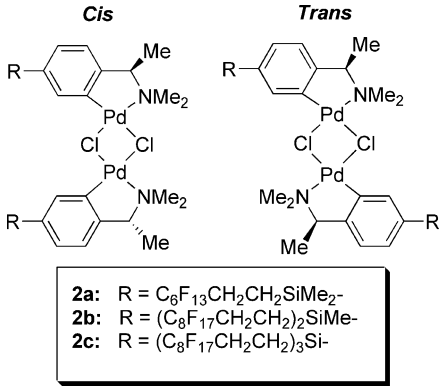



Fig. 1. *Cis* and *trans* isomers of compounds **2a**–**c**.

weakly polar solvents (e.g., chloroform), compounds **1b** and **1c** have a clear preference for more apolar environments (i.e., they have a good solubility in benzene and in hexafluorobenzene). The MALDI-TOF-MS spectra of **1a**–**1c** all showed a distinct and clear $[M + H]^+$ molecular ion in the presence of 3,5-dihydroxy-benzoic acid as matrix (Section 2).

### 3.2. Synthesis and analysis of the arylpalladium(II)chloride complexes

Earlier studies have demonstrated that functionalized benzylamine ligands (such as TMBA) are excellent precursors for preparation of the corresponding Pd(II)-complexes by a cyclometalation process that involves the reaction of the TMBA ligand with $Pd(OAc)_2$ in a protic solvent [14]. Similarly, ligands **1a**–**1c** (Scheme 1) readily reacted to yield the corresponding Pd(II) chloride complexes **2a**–**2c** in high yields (90–99%). Confirmation of their anticipated stoichiometry was provided by $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopic studies. $^1H$ NMR spectra of **2a**–**2c** showed characteristic singlet resonances for the $ArH_{ortho}$ protons in the range 7.40–7.30 ppm and two separate singlet peaks for the $NCH_3$ groups at 2.9 and 2.7 ppm, respectively. The latter observation indicated that under these conditions the N-donor atom is involved in a rigid nitrogen-to-palladium coordination resulting in a stable (on the NMR time-scale), five-membered, chelate ring. As a result the NMe protons are diastereotopic.

Interestingly, complexes **2a**–**2c** form dimeric species (Fig. 1) via halide-bridging both in solution and in the gas phase.[3] For **2a** and **2b**, the presence of a 1:1 mixture of *cis*- and *trans* dimers was noted in their respective $^{13}C$ NMR spectra: two sets of resonances corresponding to the aryl (**2a**, **2b**), *C*HMe (**2b**), diastereotopic NMe (**2a**), and CH*Me* (**2a**, **2b**) carbon atoms of each of the two isomers were observed (Section 2). However, in the case of

[3] Here, solution NMR spectroscopic studies ($^1H$ and $^{13}C\{^1H\}$) have been used to assign structures to the isomeric species observed, whereas MS (FAB, MALDI-TOF) has provided evidence that the halide-bridging is retained in the gas-phase.

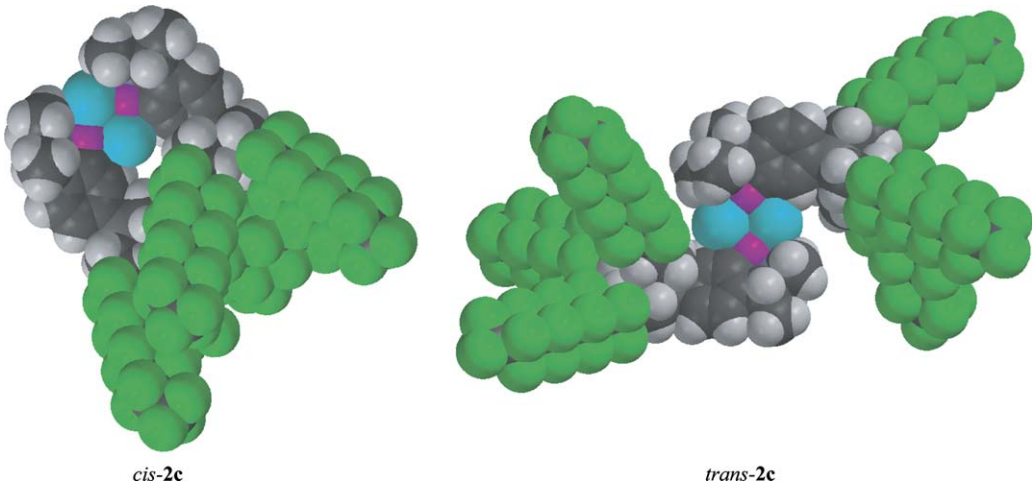



Fig. 2. Calculated structures for *cis*- (left) and *trans*-**2c** (right). Green, fluor atoms; purple, palladium atoms; turquoise, chloride atoms.

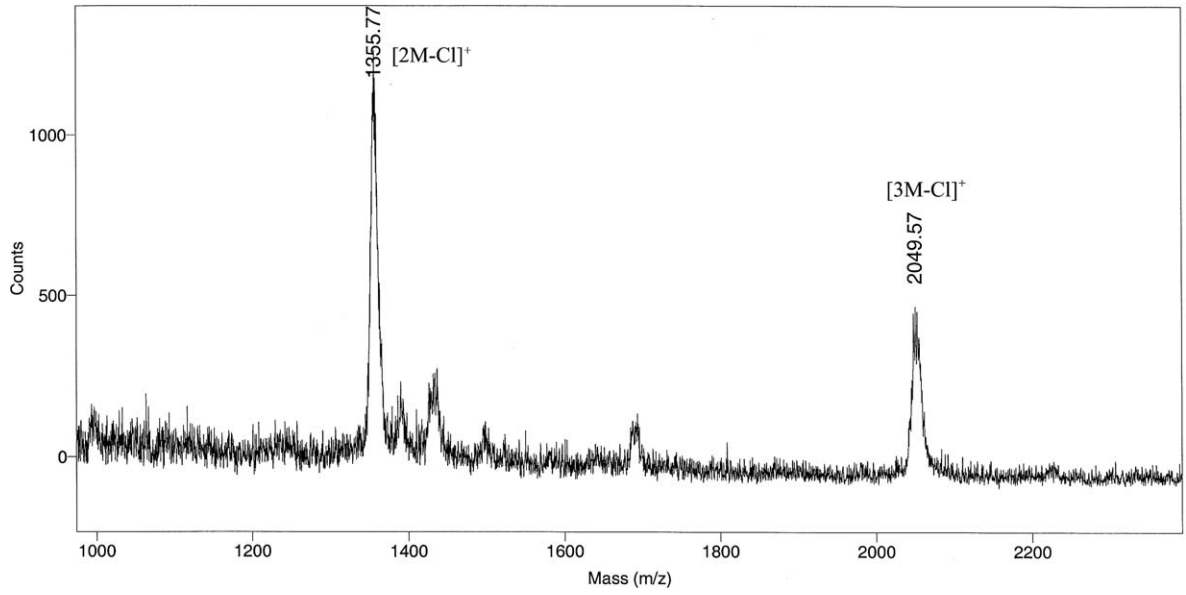



Fig. 3. MALDI-TOF-MS analysis of compound **2a**.

**2c**, the NMR spectra showed only one set of signals indicating that only one single isomer had been formed. This assumption seems to be supported by molecular modeling studies (Spartan 5.1.1, semi-empirical PM3 force field, SGI workstation), which were carried out for **2c**. It appeared that the *cis*-dimer[4] is highly unfavorable because of severe mutual steric interactions between the perfluoroalkyl chains in each of the two monomer units. On the basis of these stereo-chemical considerations, the presence of the *trans*-dimer is the most likely situation (Figs. 1 and 2).

MALDI-TOF-MS analysis (9-nitro-anthracene matrix) unequivocally supported the proposed dinuclear structures of the new Pd(II) chloride complexes. The spectra of **2a**–**2c** showed in each case an intense peak for the $[2M - Cl]^+$ fragment ions (M = (CN)PdCl), a fact that points to a strong association of the monomeric species also under gas-phase conditions (see Fig. 3). The spectra further displayed intense signals for the monomeric species (fragment ion $[M - Cl]^+$) and fragment ions derived thereof. In the case of **2a**, also a trimeric fragment $[3M - Cl]^+$ ion (2049.57) was observed (Fig. 3), a result that demonstrates that also higher order aggregates can be formed under the MS conditions [15].

### 3.3. Synthesis and analysis of pyridine and triphenylphosphine adducts

The structures of **2a**–**2c** could be further verified by bridge-splitting reactions using suitable donor ligands (e.g., pyridine or $PPh_3$). Upon addition of these ligands,

[4] The prefixes *cis* and *trans* here refer to the relative position of the two $NMe_2$ donor groups with respects to the $Pd_2Cl_2$ unit.

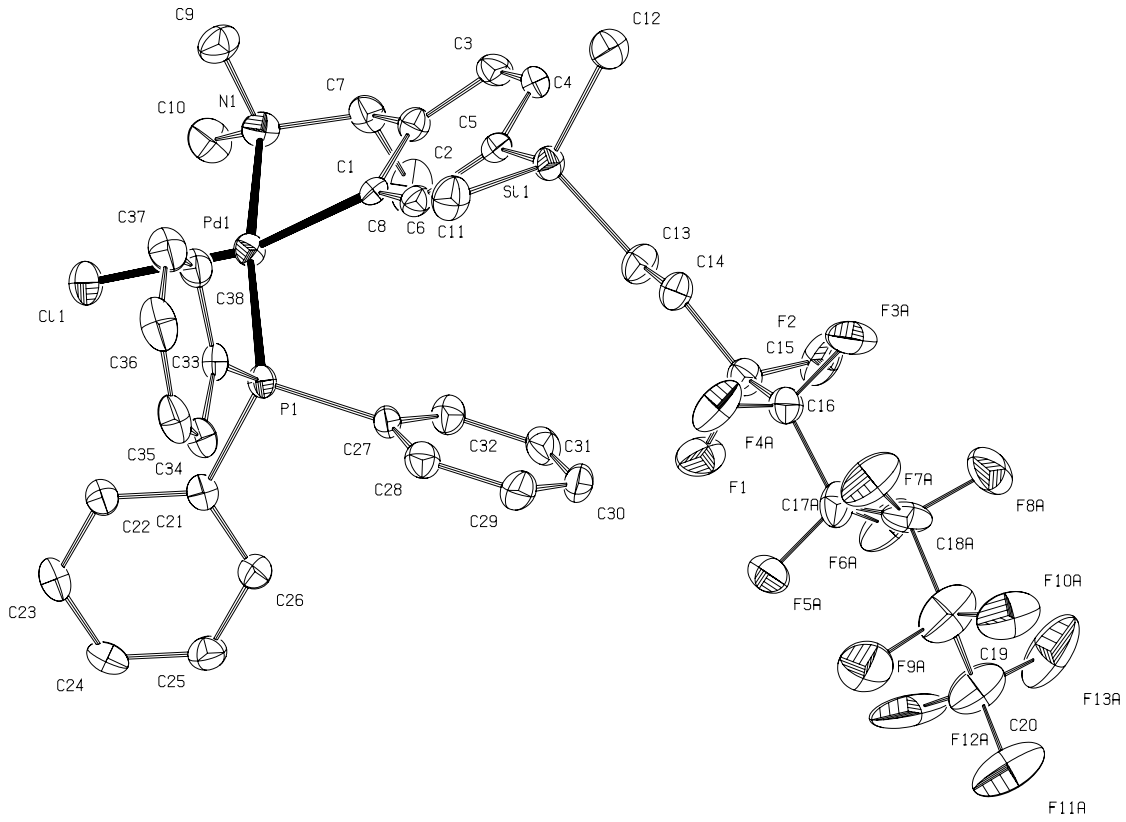



Fig. 4. Displacement ellipsoid plot of **4a**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Only the major orientation of the disordered perfluoroalkyl chain is shown.

the two sets of signals in the $^1$H NMR spectra of **2a**–**2c** (mixture of stereo-isomers) collapsed into a single, new pattern corresponding to **3a**–**3c**, respectively (Scheme 1). New signals corresponding to the pyridine ligand were noted for **3a**–**3c** at $\delta$ 8.9, 7.8 and 7.3–7.4 ppm. However, the most significant change in the $^1$H NMR spectra was the large up-field shift for the $ArH_{ortho}$ protons from *ca.* 7.31–7.36 ppm (in **2a**–**2c**) to 6.00–6.03 ppm (in **3a**–**3c**). This can be ascribed to the shielding nature of the pyridine ligand, which is *trans*-positioned with respect to the $NMe_2$ donor group in this type of complexes[5] and consequently close to the aryl H(6) proton. Small changes upon pyridine coordination for the resonances assigned to the SiMe protons were found for **2a** and **2b** (Section 2).

In contrast to the considerable upfield shift in the case of the pyridine complexes, the shielding effect of the P-aryl groups in the triphenylphosphine complexes **4a**–**4c** appeared to be much smaller. The aryl H(6) protons were found in the range 6.5–6.6 ppm. The relative orientation of the P-aryl groups seemed to be dependent of the number of perfluoro tails present in the precursor materials **2a**–**2c**, since the chemical shift values of the aryl H(6) protons changed from 6.61 (**4a**), 6.57 (**4b**) to 6.52 ppm (**4c**).

MALDI-TOF-MS spectrometric measurements performed in the series **3a**–**3c** and **4a**–**4c** revealed that these complexes quickly loose their neutral donor ligand and consequently all give rise to observation of the respective $[M - Cl - L]_n^+$ ($n = 1$, 2) fragment ion (cf., complexes **2a**–**2c**). This has also been observed with similar type of Pd(II) complexes attached to the periphery of dendrimeric supports [15].

### 3.4. Molecular Structure of *4a* in the solid state

Crystals of complex **4a** were obtained from a 1:1 volumetric mixture of *n*-octane and perfluoromethylcyclohexane.

The molecular structure of **4a** reveals clearly the *trans* arrangement of the nitrogen and phosphorous atom around a square planar palladium centre (see Fig. 4). In this *trans* P,N-arrangement the three ponytails of **4c** can be easily accommodated. This conclusion is in line with the small chemical shift differences observed for the phosphine H(6) protons in the $^1$H NMR solution spectra of the series **4a**–**4c**. **4a** crystallizes enantiomerically pure in the space group $P2_1$ with an *R*-configuration at the *C*H(Me)($NMe_2$) carbon atom.

The angles C(1)–Pd(1)–N(1) (80.81(16)°), C(1)–Pd(1)–Cl(1) (166.03(16)°) and P(1)–Pd(1)–N(1) (170.88(12)°) are

[5] The pyridine ligand is situated *trans* with respect to the $NMe_2$ donor group of the TMBA ligand supported by the large high-field shifts encountered for the $ArH_{ortho}$ of the Pd(II)Cl-complexes **1c**–**3c**. The same accounts for the $PPh_3$ complexes **1d**–**3d**. See also Ref. [18].

Table 1
Selected bond lengths (Å), bond angles and torsion angles (°) for compound **4a**

| | | | |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| Pd(1)–Cl(1) | 2.3975(12) | Pd(1)–N(1) | 2.143(4) |
| Pd(1)–C(1) | 2.024(4) | Pd(1)–P(1) | 2.2466(13) |
| *Bond angles (°)* | | | |
| C(1)–Pd(1)–P(1) | 93.44(13) | C(1)–Pd(1)–Cl(1) | 166.03(16) |
| C(1)–Pd(1)–N(1) | 80.81(16) | P(1)–Pd(1)–Cl(1) | 94.20(5) |
| P(1)–Pd(1)–N(1) | 170.88(12) | Cl(1)–Pd(1)–N(1) | 92.91(12) |
| *Torsion angles (°)* | | | |
| C(1)–C(2)–C(7)–C(8) | −87.9(6) | Cl(1)–Pd(1)–N(1)–C(9) | 83.4(3) |
| N(1)–Pd(1)–C(1)–C(2) | −15.4(4) | Cl(1)–Pd(1)–P(1)–C(21) | 37.34(18) |

severely distorted from the ideal values of 90° and 180°, respectively (see Table 1). This has also been observed previously for related Pd(II) and Pt(II) C–N-coordinated complexes (values ranging from 80.6° to 82.7° 168.2° to 170.4° and 169.5° to 178.0° have been reported) [16]. The bond lengths Pd(1)–C(1) (2.024(4) Å), Pd(1)–Cl(1) (2.3975(12) Å), Pd(1)–P(1) (2.2466(13) Å) and Pd(1)–N(1) (2.143(4) Å) are also in good agreement with the bond lengths reported for such compounds (values ranging from 1.96 to 2.03, 2.37 to 2.40, 2.23 to 2.26 and 2.10 to 2.16 Å, respectively). The perfluoroalkyl chain is disordered in the crystal structure, a phenomenon frequently encountered in crystal structures of compounds functionalized with perfluoroalkyl chains [6a,17], and bends away from the rest of the molecule. Furthermore, the distance Pd(1)–H(38) (2.89 Å) is significantly shorter than the sum of the Van der Waals radii of Pd and H (3.50 Å), indicative of a Pd–H close contact in a otherwise square planar coordination environment [18].

### 3.5. Fluorophilicity of the fluorous ligand and arylpalladium(II) complexes

The partition coefficient determinations for the different complexes and ligands were carried out in a fluorous biphasic mixture consisting of perfluoromethylcyclohexane (PFMCH) and *n*-octane at 0 °C (Section 2). This system becomes monophasic at about 37 °C and is often used for fluorous biphasic separation strategies. The values for the partition coefficient of the various complexes are clearly correlated to the number of fluorous tails that have been attached to the silicon tethering point (Table 2). Compounds with one ponytail, (**1a**, **2a**, **3a**, **4a**), preferentially dissolve in the octane layer, whereas the compounds with three ponytails, (**1c**, **2c**, **3c**, **4c**), dissolve exclusively in the PFMCH layer. Compounds with two ponytails, (**1b**, **2b**, **3b**, **4b**), still dissolve equally well in octane as in PFMCH. From the results listed in Table 2 we can also conclude that for efficient fluorous biphasic separation strategies to succeed with TMBA-based palladium(II) complexes, at least three fluorous tails are needed.

Table 2
Partition coefficients *P* of fluorous compounds **1a**,**b**,**c**–**4a**,**b**,**c**

| Entry | Compound | *P* |
|---|---|---|
| 1 | **1a** | 0.21[a] |
| 2 | **1b** | 3.93[a] |
| 3 | **1c** | 97[a] |
| 4 | **2a** | <0.003[b] |
| 5 | **2b** | 1.64[b] |
| 6 | **2c** | 33[b] |
| 7 | **3a** | 1.79[b] |
| 8 | **3b** | 14[b] |
| 9 | **3c** | 75[b] |
| 10 | **4a** | 0.007[b] |
| 11 | **4b** | 1.45[b] |
| 12 | **4c** | 21[b] |

[a] $P = C_{\text{fluorous layer}}/C_{\text{organic layer}}$ in a PFMCH/*n*-octane biphasic system at 0 °C determined by gravimetric method.
[b] $P = C_{\text{fluorous layer}}/C_{\text{organic layer}}$ in a PFMCH/*n*-octane biphasic system at 0 °C, Pd determination by ICP/AAS method.

## 4. Conclusion

In summary, we have presented synthetic procedures for the construction of chiral complexes that comprise a covalently bonded Pd(II)-center and that are potentially useful in FBS separation strategies. The properties of these Pd(II) metal centers may be altered by introduction of new ligands into the metal coordination sphere. This is illustrated by the conversion of dimeric bridged chloride **2a**–**c** into pyridine (**3a**–**3c**) or triphenylphosphine (**4a**–**4c**) adducts and may offer potential for tuning their catalytic properties. The partition coefficients show that the fluorophilicity increased markedly on increasing the number of perfluorotails with three $-C_2H_4C_8F_{17}$ tails being required to offer preferential fluorophase solubility. Currently suitable catalytic applications employing fluorous biphasic conditions are under investigation.

## 5. Supplementary data

Crystallographic data for this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 283244 (**4a**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 3360333 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgement

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