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Synthesis, molecular structures, and chemistry of some new palladium(II) and platinum(II) complexes with pentafluorophenyl ligands

Russell P. Hughes,*[a] Antony J. Ward,[a] James A. Golen,[b] Christopher D. Incarvito,[c] Arnold L. Rheingold[d] and Lev N. Zakharov[d]

[a] *Department of Chemistry, Dartmouth College, 6128 Burke Laboratory, Hanover, New Hampshire 03755 USA. E-mail: rph@dartmouth.edu; Tel: +603-646-2763*

[b] *Department of Chemistry, University of Massachusetts Dartmouth, North Dartmouth, MA 02747 USA*

[c] *Department of Chemistry, Yale University, New Haven, 06520-8107 USA*

[d] *Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0358 USA*

Received 4th May 2004, Accepted 16th June 2004
First published as an Advance Article on the web 23rd July 2004

A series of palladium(II) and platinum(II) complexes possessing pentafluorophenyl ligands of the general formula [M(L–L)(C_6F_5)Cl] (M = Pd **3**; L–L = tmeda (*N*,*N*,*N′*,*N′*,-tetramethylethylenediamine) **a**; 1,2-bis(2,6-dimethylphenylimino)ethane) **b**; dmpe (1,2-bis(dimethylphosphino)ethane) **c**; dcpe (1,2-bis(dicyclohexylphosphino)ethane) **d**; Pt **4**; L–L = tmeda **a**; 1,2-bis[3,5-bis(trifluoromethyl)phenylimino]-1,2-dimethylethane **b**; dmpe **c**; dcpe **d**) were readily synthesized from the dimer [M(C_6F_5)(tht)(μ-Cl)$_2$] (M = Pd **1b**, Pt **2b**; tht = tetrahydrothiophene) and the corresponding bidentate ligand. In the case of palladium, the corresponding iodo analogues (**6a**–**c**) were readily synthesized in a one-pot reaction from [Pd_2(dba)$_3$], iodopentafluorobenzene, and the appropriate ligand. The platinum complexes **4c**–**d** were then converted to the water complexes [Pt(L–L)(C_6F_5)(OH_2)]OTf (L–L = dmpe **7a**; dcpe **7b**) *via* reaction with AgOTf in the presence of water. Attempts to convert the palladium complexes **3c**–**d** to the corresponding water complexes resulted in the disproportionation of the intermediate water complex to form [Pd(L–L)(C_6F_5)$_2$] (L–L = dmpe **8**) or [Pd(L–L)$_2$][OTf]$_2$ (L–L = dcpe **9**). Upon standing in solution for prolonged periods, complex **7a** undergoes an identical disproportionation reaction to the Pd analogues to form [Pt(L–L)(C_6F_5)$_2$] (L–L = dmpe **10**). Complexes **4c** and **4d** were converted to the corresponding hydrides (**11b**–**c**, respectively) using two different hydride sources: **11a** was formed by the reaction of **4c** with $NaBH_4$ in refluxing THF, while **11b** was synthesized in near quantitative yield using [Cp_2ZrH_2] in refluxing THF. Attempts to synthesize η^2-tetrafluorobenzyne complexes [Pt(L–L)(C_6F_4)] (L–L = dmpe, dcpe) from reaction of **11a**–**b** with butyllithium were unsuccessful. The molecular structures of **3a**, **4a**, **4c**, **4d**, **6b**, **7a**, **8**, and **11b** have been determined by X-ray crystallographic studies, and are discussed.

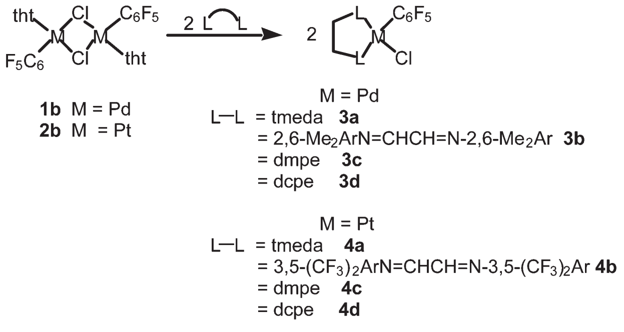
Introduction

Recent work within our research group has shown that treatment of [Cp*Ir(PMe_3)(C_6F_5)H] with excess *n*-butyllithium resulted in the formation of the first transition metal-η^2-tetrafluorobenzyne complex [Cp*Ir(PMe_3)(C_6F_4)].[1] This reaction scheme, involving apparent deprotonation of the hydride and elimination of an *ortho*-fluorine, proved to be a general route to partially fluorinated and non-fluorinated benzyne complexes of iridium and rhodium.[2,3] In seeking to expand the applicability of this reaction to the preparation of fluorinated benzyne complexes of other metals, we sought routes to other hydrido(pentafluorophenyl)metal complexes. Since benzyne complexes of palladium and platinum are well-known,[4–7] these metals seemed like good choices. In addition, a large body of work concerning pentahalophenyl derivatives of palladium and platinum[8] has resulted in characterization of several precursors for the synthesis of a large variety of complexes possessing these aryl ligands.[9–15] In this paper we describe the syntheses of several platinum and palladium complexes containing pentafluorophenyl ligands as potential, albeit unsuccessful, precursors for fluorinated benzyne complexes.

Results and discussion

Halo complexes

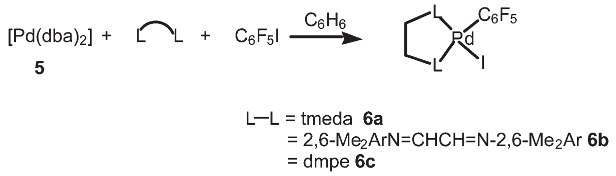
The dimeric complexes [M(C_6F_5)$_2$(tht)$_2$(μ-Cl)$_2$] (tht = tetrahydrothiophene; M = Pd **1**, Pt **2**) undergo ready displacement of tht by the appropriate chelating ligand to afford complexes [M(L–L)(C_6F_5)Cl] (M = Pd; L–L = tmeda **3a**, 2,6-Me_2ArN=CHCH=N-2,6-Me_2Ar **3b**, dmpe **3c**, dcpe **3d**: M = Pt; L–L = tmeda **4a**, 3,5-(CF_3)$_2$ArN=C(CH_3)C(CH_3)=N-3,5-(CF_3)$_2$Ar **4b**, dmpe **4c**, dcpe **4d**) as shown in Scheme 1. In the case of the Pd complexes, stirring the dimer in THF in the presence of the ligand at room temperature is sufficient to form the desired mononuclear complexes, but formation of the analogous platinum complexes required heating a chloroform (or toluene) solution of the dimer and the ligand.



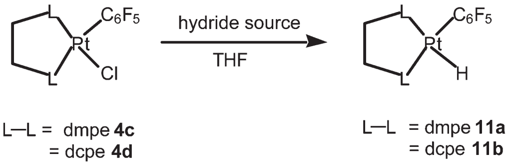
Scheme 1

A second synthetic route is also available to form iodo analogues of the Pd complexes. This is a ‘one-pot’ synthesis that involves heating a benzene solution of [Pd(dba)$_2$] (dba = dibenzylideneacetone) **5** in the presence of the appropriate ligand and C_6F_5I as shown in Scheme 2.

DOI: 10.1039/b406602b



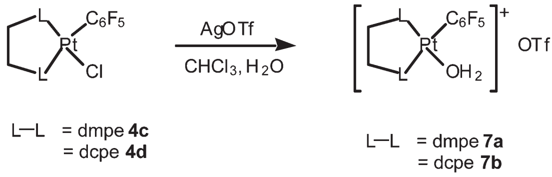
Scheme 2



Scheme 4

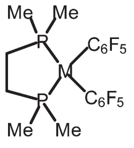
The yields after recrystallization are generally good except when phosphine ligands are used: in these cases the C_6F_5I is apparently sufficiently electrophilic to react with the free phosphine, so yields of the desired complexes are low and the product is difficult to purify. Low yields were also observed when the [Pd(dmpe)(dba)] complex was formed *in situ* prior to addition of the C_6F_5I.

Water complexes of Pt were readily synthesized in moderate yields by slow addition of the halo complex to a suspension of AgOTf in chloroform at room temperature as shown in Scheme 3.

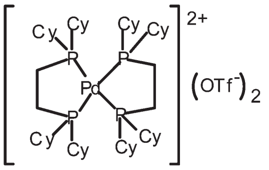


Scheme 3

The complexes were obtained as white powders upon precipitation. Attempts to make the analogous palladium water complexes from **3c** or **3d** proved unsuccessful due to apparent disproportionation reactions, which occurred before any water complex could be isolated. When dmpe was the chelate ligand the only isolable product from reaction of **3c** was $[Pd(dmpe)(C_6F_5)_2]$ (**8**), while the corresponding reaction of **3d** afforded only $[Pd(dcpe)_2][OTf]_2$ (**9**). The fate of the missing pentafluorophenyl groups or excess palladium has not been determined. In the case of platinum complex **7a** the analogous disproportionation reaction occurs at a significantly slower rate, taking 3 weeks of stirring at room temperature in $CHCl_3$ to form $[Pt(dmpe)(C_6F_5)_2]$ **10**. In the case of the dcpe complex **7b** no reaction was observed after stirring the complex at room temperature for 3 weeks. Authentic samples of complexes **8** and **10** were synthesized independently in order to confirm their formation in the disproportionation reactions. Addition of dmpe to a THF solution of $[M(C_6F_5)_2(tht)_2]$ (M = Pd **1**; Pt **2**) afforded the desired complexes in high yields.



8 M = Pd
10 M = Pt



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Hydride complexes

The syntheses of the target hydride complexes was successful in only two cases to give platinum complexes **11a** and **11b**, and required different hydride sources for the different precursors. Attempts to make the complex $[Pt(tmeda)(C_6F_5)H]$ from **4a** using hydride sources such as $NaBH_4$, $LiEt_3BH$, and $[Cp_2ZrH_2]$ resulted in complete decomposition of the starting material, while heating **4a** in the presence of $NaBH_3CN$ in THF resulted in no observable reaction. Likewise, the synthesis of **11a** from the water complex **7a** and Proton Sponge® was also attempted, but no reaction was observed, in contrast to the high yield synthesis of hydrido-iridium complexes using this approach.[16] A successful synthesis of $[Pt(dmpe)(C_6F_5)H]$ **11a** was only achieved in modest yield (59%) using $NaBH_4$; when $[Cp_2ZrH_2]$ was used, multiple products were obtained that could not be separated. In contrast, the hydride $[Pt(dcpe)(C_6F_5)H]$ **11b** was obtained in 98% yield when a THF solution of **4d** was stirred with 1 equivalent of $[Cp_2ZrH_2]$ at room temperature. Despite numerous attempts using different hydride sources (such as $NaBH_4$, $LiBHEt_3$, and $[Cp_2ZrH_2]$), no Pd hydride complexes could be synthesized.

The hydrido compounds were readily identified using NMR, with the hydride resonance for **11a** appearing as a doublet of doublet of multiplets at δ −1.48 ppm, with $^2J_{\mathrm{P}(cis)\mathrm{H}} = 17$ Hz, $^2J_{\mathrm{P}(trans)\mathrm{H}} = 200$ Hz, and $^1J_{\mathrm{PtH}} = 1080$ Hz. Similarly, the hydride resonance for **11b** appears as a doublet of doublet of multiplets at δ −0.30 ppm, with $^2J_{\mathrm{P}(cis)\mathrm{H}} = 4.5$ Hz, $^2J_{\mathrm{P}(trans)\mathrm{H}} = 165$ Hz and a Pt–H coupling constant of 1036 Hz. The multiplet component of the resonances arises from the coupling of the hydride with the AA′MM′X spin system of the C_6F_5 ligand.

As stated in the Introduction, the ultimate aim of this work was to synthesize tetrafluorobenzyne complexes utilizing the dehydrofluorination protocol that was recently developed within this research group.[1–3] Unfortunately this methodology proved unsuccessful using the only two hydrides **11a**,**b**. Treatment of **11a** with excess *n*-butyllithium in hexane at room temperature for 24 h resulted in decomposition with no resonances attributable to the desired η^2-tetrafluorobenzyne complex present. In the case of **11b**, the dcpe ligand appears to be too large to allow the abstraction of the hydride by either *n*-butyllithium or *t*-butyllithium, and starting material was obtained after the reaction was worked-up.

Despite this disappointing outcome to our synthetic aspirations, a number of new pentafluorophenyl complexes resulted from these studies. Several have been characterized by X-ray crystallography, and show some interesting features, described below.

Structural studies

The structures of complexes **3a** (Fig. 1), **4a** (Fig. 2), **4c** (Fig. 3), **4d** (Fig. 4) and **6b** (Fig. 5) were determined by X-ray crystallography. In each case, X-ray diffraction quality crystals were grown by the slow infusion of hexanes into a CH_2Cl_2 solution of the complex. In two cases the crystals included a half (**4c**) or whole (**4d**) molecule of CH_2Cl_2 in the lattice, not included in the ORTEP diagrams. Details of all crystal structure determinations are presented in Table 1. Selected bond lengths and angles for the coordination sphere of the metal in each compound are presented in Table 2. To make for easy comparison a common numbering system is used with atom X(1) (X = Cl, I, H, OH_2) always *trans* to L(2) (L = N, P), and atom C(1) (the coordinated carbon of the C_6F_5 moiety) always *trans* to L(1).

In the case of the palladium complexes **3a** and **6b**, the observed Pd–C(1), Pd–N(1), and Pd–N(2) bond lengths are close to identical. Such comparisons for the Pt complexes **4a**, **4c**, and **4d** cannot be drawn due to the different coordinating atoms of the ligands. The *trans*-influence is clearly illustrated when comparing the M–L(1) and M–L(2) bond lengths: in all cases, the M–L(2) bond length is longer than the M–L(1) bond length, indicating that a stronger *trans*-influence is exerted by the C_6F_5 group than by the halide. The crystal structures of all complexes show that the pentafluorophenyl moiety subtends an angle of approximately 85° to the plane formed by the metal, bidentate ligand and the halide.

X-ray diffraction quality crystals of **7a** were grown from the slow infusion of hexanes into a solution of CH_2Cl_2 containing the complex. The structure contains four independent molecules in the asymmetric unit; the ORTEP diagram of one is shown in Fig. 6. The X-ray structure shows the complex to be planar, with the C_6F_5 group subtending an angle of approximately 85° with the plane formed by the Pt, the 2 phosphorus atoms, and the O. The bond lengths for the coordination sphere of the metal show that the C_6F_5 groups exerts a stronger *trans*-influence than the coordinated water molecule

Table 1 Summary of X-ray crystallographic data collection, solution, and refinement parameters for **3a**, **4a**, **4c**, **4d**, **6b**, **7a**, **10**, and **11b**

Complex	**3a**	**4a**	**4c**·0.5CH$_2$Cl$_2$	**4d**·CH$_2$Cl$_2$	**6b**	**7a**	**10**	**11b**
Formula	$C_{12}H_{16}ClF_5N_2Pd$	$C_{12}H_{16}ClF_5N_2Pt$	$C_{12.5}H_{17}C_{l2}F_5P_2Pt$	$C_{33}H_{50}Cl_3F_5P_2Pt$	$C_{24}H_{20}F_5IN_2Pd$	$C_{13}H_{18}F_8O_4P_2PtS$	$C_{18}H_{16}F_{10}P_2Pd$	$C_{32}H_{49}F_5P_2Pt$
M	425.12	513.81	590.19	905.11	664.72	679.36	590.65	785.74
Space group	$Aba2$	$Aba2$	$Pbca$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	12.562(4)	12.6158(6)	12.8842(7)	10.7702(5)	7.2890(4)	15.5771(16)	19.849(2)	10.3469(6)
b/Å	19.871(7)	19.9069(9)	11.8461(6)	14.5259(7)	8.4947(5)	17.1317(17)	8.5944(8)	10.5606(6)
c/Å	12.038(4)	12.0280(6)	23.6481(12)	23.0871(11)	20.2669(12)	17.5578(18)	13.0998(13)	16.5159(9)
α/°	90.00	90.00	90.00	90.00	100.9760(10)	89.841(2)	90.00	72.5620(10)
β/°	90.00	90.00	90.00	97.1180(10)	91.4360(10)	72.818(2)	110.1530(10)	76.3330(10)
γ/°	90.00	90.00	90.00	90.00	103.0630(10)	72.046(2)	90.00	69.0590(10)
V/Å^3	3005.0(17)	3020.7(2)	3609.4(3)	3584.1(3)	1197.00(12)	4238.3(7)	2097.9(4)	1591.03(6)
Z	8	8	8	4	2	8	4	2
μ/mm^{-1}	1.460	9.514	8.439	4.28	2.118	6.957	1.127	4.560
T/K	173(2)	173(2)	173(2)	150(2)	203(2)	100(2)	147(2)	100(2)
Total data	6772	9218	21042	22322	14193	27052	6191	10121
Unique data [R_{int}]	2870 [0.0500]	2814 [0.0410]	4291 [0.0331]	8313 [0.0282]	5620 [0.0307]	18980 [0.0352]	2400 [0.0281]	7142 [0.0243]
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0443, 0.1019	0.0259, 0.0563	0.0263, 0.0775	0.0241, 0.0581	0.0295, 0.0717	0.0860, 0.2501	0.0262, 0.0637	0.0330, 0.0779
(all data)	0.0675, 0.1147	0.0300, 0.0632	0.0316, 0.0863	0.0282, 0.0594	0.0358, 0.0750	0.1282, 0.2648	0.0283, 0.0650	0.0370, 0.0796

Table 2 Selected bond lengths (Å) and angles (°) in the coordination sphere of the metal in **3a**, **4a**, **4c**, **4d**, **6b**, **7a**, **10**, and **11b**

Complex	**3a**	**4a**	4c·0.5CH$_2$Cl$_2$	4d·CH$_2$Cl$_2$	**6b**	**7a**[a]				**8**[b]	**11b**
M–C(1)	1.984(7)	1.994(6)	2.079(4)	2.086(3)	1.990(3)	2.081(16)	2.079(19)	2.090(17)	2.106(18)	2.079(2)	2.067(4)
M–L(1)	2.125(6)	2.112(5)	2.2713(11)	2.2764(7)	2.111(2)	2.280(5)	2.268(5)	2.277(5)	2.252(5)	2.2653(6)	2.2379(10)
M–L(2)	2.075(6)	2.064(5)	2.2034(11)	2.2212(7)	2.070(2)	2.187(5)	2.196(5)	2.192(5)	2.187(5)	2.2653(6)	2.3007(11)
M–X	2.302(2)	2.3079(17)	2.3849(10)	2.3674(7)	2.5520(3)	2.122(11)	2.174(10)	2.109(11)	2.148(12)	2.079(2)	1.68(6)
C(1)–M–L(1)	178.4(3)	178.8(2)	176.42(12)	174.85(8)	172.02(10)	174.3(5)	178.4(5)	175.8(5)	177.0(5)	89.86(6)	174.23(11)
C(1)–M–L(2)	93.4(3)	94.2(2)	94.59(11)	95.54(7)	94.10(10)	94.2(5)	95.7(5)	93.9(5)	95.9(5)	175.56(6)	98.01(12)
C(1)–M–X	88.1(2)	88.23(18)	91.30(11)	85.59(7)	87.53(8)	87.2(6)	85.0(6)	86.4(5)	84.2(5)	94.46(11)	82(2)
L(1)–M–L(2)	85.2(2)	84.6(2)	85.83(4)	87.63(2)	78.19(9)	85.44(17)	85.76(17)	85.70(17)	86.32(18)	85.83(3)	87.71(4)
L(1)–M–X	93.19(18)	92.93(14)	88.42(4)	91.10(2)	100.33(6)	93.4(3)	93.5(4)	94.1(3)	93.7(3)	89.86(6)	92(2)
L(2)–M–X	178.43(18)	177.57(14)	173.77(4)	177.77(2)	174.70(6)	178.3(4)	179.2(4)	179.8(4)	176.5(4)	175.56(6)	179(2)

[a] 4 independent molecules in the asymmetric unit. [b] Molecule lies on a two-fold crystallographic axis, X = C$_6$F$_5$.

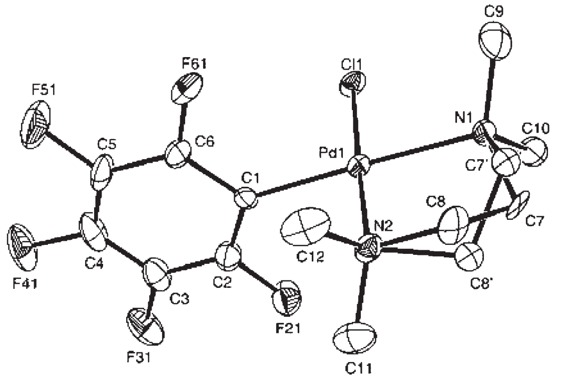

Fig. 1 ORTEP diagram of the non-hydrogen atoms of **3a**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

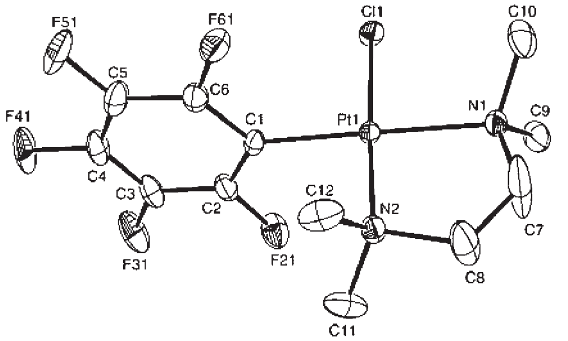

Fig. 2 ORTEP diagram of the non-hydrogen atoms of **4a**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability. Only one position of the disordered C(7), C(8) atoms is shown.

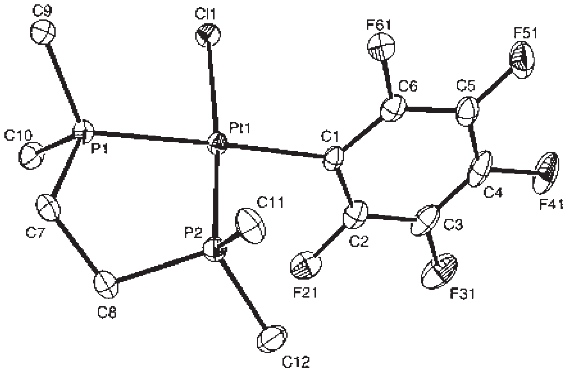

Fig. 3 ORTEP diagram of the non-hydrogen atoms of **4c**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

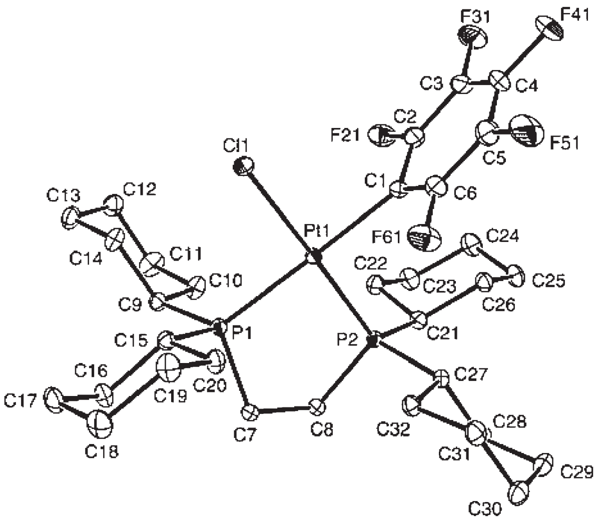

Fig. 4 ORTEP diagram of the non-hydrogen atoms of **4d**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

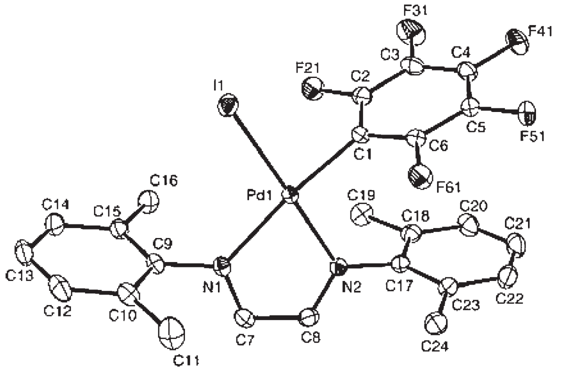

Fig. 5 ORTEP diagram of the non-hydrogen atoms of **6b**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

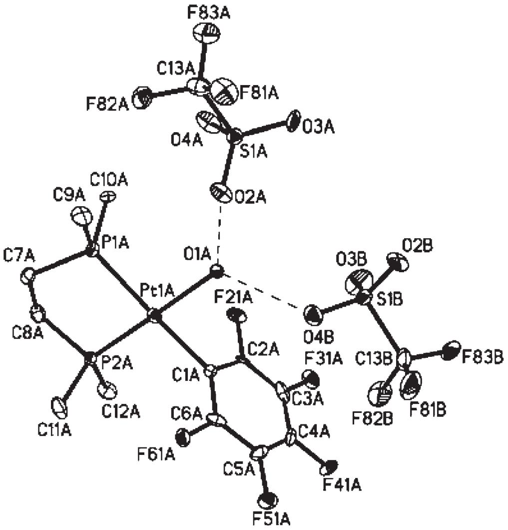

Fig. 6 ORTEP diagram of the non-hydrogen atoms of **7a**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

resulting in a longer Pt–P(2) bond length of 2.280 Å (compared to 2.187 Å for the Pt–P(1) bond). The angles show deviations from the ideal, however, this presumably results from the bite angle of the bidentate phosphine. Although the H atoms on the coordinated water molecules were not found from the F-map the found intermolecular O···O distances (2.61–2.76 Å) indicate the existence of strong O–H···O H-bonds between the water molecule and the O_3SCF_3 groups for all four independent molecules.

An X-ray diffraction quality crystal of $[Pd(dmpe)(C_6F_5)_2$ **8** was also obtained. The ORTEP diagram of **8** is shown in Fig. 7. In the crystal structure the molecule has C_2 symmetry; the Pd(1) atom and the middle of the C(7)–C(7a) bond are on a 2-fold axis. The complex is almost planar about the Pd center; the dihedral angle between the C(1)Pd(1)C(1a) and P(1)Pd(1)P(1a) planes is 1.46(9)°.

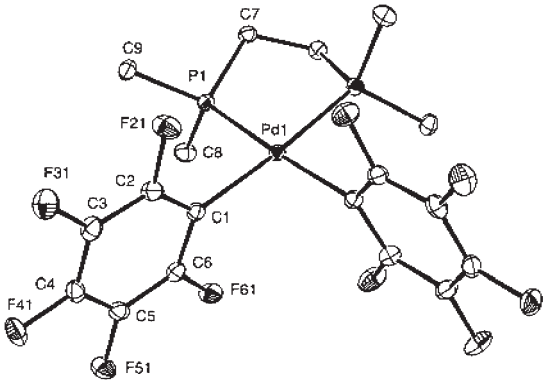

Fig. 7 ORTEP diagram of the non-hydrogen atoms of **8**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

X-ray diffraction quality crystals of **11b** were obtained by the slow evaporation of a benzene solution of the complex. The numbering system utilized is consistent with that used previously. An ORTEP diagram of **11b** is shown in Fig. 8. The metal complex is planar about the Pt center with the C_6F_5 moiety subtending an angle of approximately 85° with the plane defined by the Pt, the 2 phosphorus atoms and the hydride. The hydride ligand exerts a larger *trans*-influence than the C_6F_5 ligand resulting in a significantly longer Pt–P(1) bond than the Pt–P(2) bond (2.3006 Å compared to 2.2383 Å). Deviations from ideal angles are observed, however, this is the result of the bite angle of the phosphine ligand.

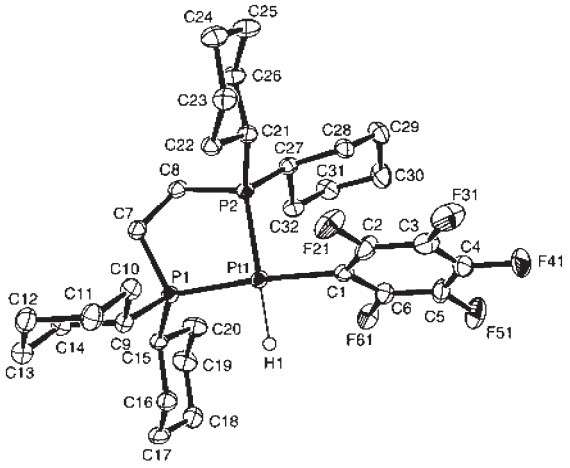

Fig. 8 ORTEP diagram of the non-hydrogen atoms (with the exception of H1) of **11b**, showing the atom labelling scheme. Thermal ellipsoids shown at 30% probability.

Experimental

General considerations

Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which had been deoxygenated over BASF catalyst and dried using Aquasorb®. Solvents were deoxygenated and dried over activated alumina using an apparatus modified from that described in literature.[17] ^1H (300 MHz), ^{19}F (282 MHz) and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian Unity-300 spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of TMS (^1H, referenced to solvent) or internal $CFCl_3$ (^{19}F). Coupling constants are reported in Hertz. Microanalyses were performed by Schwartzkopf Microanalytical Laboratory (Woodside, NY).

Bromo- and iodopentafluorobenzene were purchased from Aldrich and used without further purification. The ligands 1,2-*bis*(dimethylphosphino)ethane (dmpe) and 1,2-*bis*(dicyclohexylphosphino)ethane (dcpe) were purchased from Strem and used without further purification. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (tmeda) was purchased from Aldrich and was distilled from KOH before use. The complexes $[M(C_6F_5)_2(tht)_2]$ (M = Pd **1a**, Pt **2a**),[12] $[M_2(C_6F_5)_2(tht)_2(\mu\text{-}Cl)_2]$ (M = Pd **1b**, Pt **2b**),[12,13] $[Pd(dba)_2]$ **5**,[18] and $[Cp_2ZrH_2]$[19] were prepared according to published literature methods. The diimine ligands 1,2-*bis*(2,6-dimethylphenylimino)ethane[20] and 1,2-*bis*[3,5-*bis*(trifluoromethyl)phenylimino]-1,2-dimethylethane[21] were synthesized using published literature methods.

[1,2-bis(dimethylamino)ethane](chloro)pentafluorophenylpalladium(II) 3a. To a solution of **1b** (100 mg, 0.13 mmol) in THF (10 mL) was added tmeda (38 µL, 0.26 mmol) and the reaction was heated at reflux for 2 h. The solution was cooled and stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was extracted with hexane to afford the product as a pale yellow powder (88 mg, 82%). ^1H NMR ($CDCl_3$): δ 2.82–2.69 (m, 4H, NCH_2), 2.77 (s, 6H, NCH_3), 2.63 (s, 6H, NCH_3) ppm. ^{19}F NMR ($CDCl_3$): δ −121.02 (m, 2F, *o*-ArF), −160.45 (dd, 1F, $^3J_{FF}$ = 20 Hz, $^4J_{FF}$ = 20 Hz, *p*-ArF), −163.24 (m, 2F, *m*-ArF) ppm. Anal. Calcd. for $C_{12}H_{16}ClF_5N_2Pd$: %C, 33.90; %H, 3.80. Found: %C, 34.05; %H, 3.65.

[1,2-bis(2,6-dimethylphenylimino)ethane](chloro)pentafluorophenylpalladium(II) 3b. To a solution of **1b** (100 mg, 0.13 mmol) in THF (10 mL) was added 1,2-*bis*(2,6-dimethylphenylimino)ethane (66 mg, 0.25 mmol) and the reaction mixture was stirred at room temperature overnight. The solvent was reduced in volume to 5 mL *in vacuo* and hexane was added. The solution was cooled to −30 °C. Filtration afforded the product as a bright orange microcrystalline powder (80 mg, 56%). ^1H NMR ($CDCl_3$): δ 8.19 (s, 2H, N=C**H**), 7.20 (m, 2H, *m*-Ar**H**), 7.05 (m, 2H, 2 × *p*-Ar**H**), 6.95 (m, 2H, *m*-Ar**H**), 2.46 (s, 6H, 2 × ArC**H**$_3$), 2.31 (s, 6H, 2 × ArC**H**$_3$) ppm. ^{19}F NMR ($CDCl_3$): δ −119.28 (m, 2F, *o*-Ar**F**), −160.67 (t, 1F, $^3J_{FF}$ = 19 Hz, *p*-Ar**F**), −163.85 (m, 2F, *m*-Ar**F**) ppm. Anal. Calcd. for $C_{24}H_{20}ClF_5N_2Pd$: %C, 50.28; %H, 3.52. Found: %C, 50.49; %H, 3.48.

[1,2-bis(dimethylphosphino)ethane](chloro)(pentafluorophenyl)palladium(II) 3c. To a solution of **1b** (150 mg, 0.19 mmol) in THF (10 mL) at 0 °C was added a solution of dmpe (63 µL, 0.38 mmol) in THF (5 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was washed with hexane. Filtration afforded the product as a white powder (163 mg, 94%). ^1H NMR ($CDCl_3$): δ 2.14–1.88 (m, 4H, PC**H**$_2$), 1.73 (d, 6H, $^2J_{PH}$ = 11 Hz, PC**H**$_3$), 1.55 (d, 6H, $^2J_{PH}$ = 12 Hz, PC**H**$_3$) ppm. ^{19}F NMR ($CDCl_3$): δ −117.23 (m, 2F, *o*-Ar**F**), −160.06 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-Ar**F**), −162.53 (m, 2F, *m*-Ar**F**) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.1 (m, P *trans* to Cl), 42.7 (m, P *trans* to C_6F_5) ppm. Anal. Calcd. for $C_{12}H_{16}ClF_5Pd.0.5CH_2Cl_2$: %C, 29.93; %H, 3.42. Found: %C, 30.43; %H, 3.57.

[1,2-bis(dicyclohexylphosphino)ethane](chloro)(pentafluorophenyl)palladium(II) 3d. To a solution of **1b** (100 mg, 0.13 mmol) in THF (10 mL) was added a solution of dcpe (109 mg, 0.26 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue extracted with hexanes. Filtration afforded the product as a white powder (180 mg, 98%). ^1H NMR ($CDCl_3$): δ 2.32 (m, 2H, PC**H**$_2$), 2.10–1.62 (m, 22H, PC$_6$**H**$_{11}$), 1.60–1.12 (m, 22H, PC$_6$**H**$_{11}$), 0.87 (m, 2H, PC**H**$_2$) ppm. ^{19}F NMR ($CDCl_3$): δ −115.82 (m, 2F, *o*-Ar**F**), −161.06 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-Ar**F**), −162.95 (m, 2F, *m*-Ar**F**) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 83.74 (s, P *trans* to Cl), 76.52 (m, P *trans* to C_6F_5) ppm. Anal. calcd. for $C_{32}H_{48}ClF_5P_2Pd.0.75CH_2Cl_2$: %C, 49.45; %H, 6.28. Found: %C, 49.39; %H, 6.34.

[1,2-bis(dimethylamino)ethane](chloro)(pentafluorophenyl)platinum(II) 4a. To a solution of **2b** (100 mg, 0.10 mmol) in chloroform (10 mL) was added tmeda (47 µL, 0.31 mmol). The reaction mixture was heated at reflux for 1 h, then stirred overnight at room temperature. The solvent was reduced in volume *in vacuo* to 5 mL and hexane was added. Filtration afforded the product as a white microcrystalline powder (195 mg, 92%). ^1H NMR ($CDCl_3$): δ 2.93 (s, 6H, $^3J_{PtH}$ = 17 Hz, NC**H**$_3$), 2.96–2.87 (m, 2H, NC**H**$_2$), 2.86–2.75 (m, 2H, NC**H**$_2$), 2.86 (s, 6H, $^3J_{PtH}$ = 42 Hz, NC**H**$_3$) ppm. ^{19}F NMR ($CDCl_3$): δ −121.71 (m, 2F, $^3J_{PtF}$ = 344 Hz, *o*-ArF), −162.06 (m, 1F, *p*-ArF), −164.37 (m, 2F, *m*-Ar**F**) ppm. Anal. Calcd. for $C_{12}H_{16}ClF_5N_2Pt$: %C 28.05; %H 3.14. Found: %C 28.01; %H 3.11. X-Ray diffraction quality crystals were grown from CH_2Cl_2/hexane.

{1,2-bis[3,5-bis(trifluoromethyl)phenylimino]-1,2-dimethylethane}(chloro)(pentafluorophenyl)platinum(II) 4b. To a solution of **2b** (100 mg, 0.10 mmol) in toluene (10 mL) was added 1,2-*bis*[3,5-*bis*(trifluoromethyl)phenylimino]-1,2-dimethylethane (110 mg, 0.22 mmol) in $CHCl_3$ (10 mL). The reaction mixture was heated at reflux for 1 h and then stirred overnight at room temperature. The solvent was removed *in vacuo*. Recrystallization from CH_2Cl_2/hexane afforded the product as an orange microcrystalline powder (67 mg, 36%). ^1H NMR ($CDCl_3$): δ 7.97 (s, 1H, *p*-Ar**H**), 7.75 (s, 1H, *p*-Ar**H**), 7.74 (s, 2H, *o*-Ar**H**), 7.45 (s, 2H, *o*-Ar**H**), 2.17 (s, 3H, N=C(C**H**$_3$)), 1.71 (s, 3H, N=C(C**H**$_3$)) ppm. ^{19}F NMR (CDCl$_3$): δ −63.15 (s, 6F, CF$_3$), −63.65 (s, 6F, CF$_3$), −121.45 (m, 2F, $^3J_{PtF}$ = 317 Hz, *o*-Ar**F**), −160.26 (m, 1F, *p*-Ar**F**), −163.85 (m, 2F, *m*-Ar**F**) ppm. Anal. Calcd. for $C_{26}H_{12}ClF_{17}N_2Pt$: %C, 34.47; %H, 1.34. Found: %C, 34.26; %H, 1.36.

[1,2-bis(dimethylphosphino)ethane](chloro)(pentafluorophenyl)platinum(II) 4c. To a solution of **2b** (100 mg, 0.10 mmol) in chloroform (10 mL) was added a solution of dmpe (40 µL, 0.24 mmol) in toluene (10 mL) and the reaction mixture was heated at reflux for 1 h, then stirred at room temperature overnight. The solvent was removed *in vacuo*. The residue was recrystallized form CHCl$_3$/hexane to afford the product as a white powder (108 mg, 96%). ^{1}H NMR (CDCl$_3$): δ 2.08–1.75 (m, 4H, PC**H**$_2$), 1.76 (d, 6H, $^2J_{PH}$ = 11 Hz, $^3J_{PtH}$ = 22 Hz, PC**H**$_3$), 1.62 (d, 6H, $^2J_{PH}$ = 12 Hz, $^3J_{PtH}$ = 22 Hz, PC**H**$_3$) ppm. ^{19}F NMR (CDCl$_3$): δ −119.22 (m, 2F, $^3J_{PtF}$ = 140 Hz, *o*-Ar**F**), −161.06 (m, 1F, $^3J_{FF}$ = 20 Hz, $^3J_{FF}$ = 20 Hz, *p*-Ar**F**), −163.26 (m, 2F, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 35.79 (m, $^1J_{PtP}$ = 1117 Hz, P *trans* to C$_6$F$_5$), 23.43 (d, $^1J_{PtP}$ = 1798 Hz, $^3J_{PP}$ = 5 Hz, P *cis* to C$_6$F$_5$) ppm. Anal. Calcd. for $C_{12}H_{16}ClF_5P_2Pt.0.75CH_2Cl_2$: %C, 25.04; %H, 2.89. Found: %C, 25.34; %H, 2.91. X-Ray diffraction quality crystals were grown from CH$_2$Cl$_2$/hexane.

[1,2-bis(dicyclohexylphosphino)ethane](chloro)(pentafluorophenyl)platinum(II) 4d. To a solution of **2b** (200 mg, 0.21 mmol) in chloroform (10 mL) was added a solution of dcpe (183 mg, 0.43 mmol) in toluene (10 mL) and the reaction mixture was heated at reflux for 1 h, then stirred at room temperature overnight. The solvent was reduced in volume *in vacuo* to 5 mL and hexane was added. Filtration afforded the product as a white powder (325 mg, 96%). ^{1}H NMR (CDCl$_3$): δ 2.48–2.20 (m, 4H, PC**H**$_2$), 2.08–1.12 (m, 44H, PC$_6$**H**$_{11}$) ppm. ^{19}F NMR (CDCl$_3$): δ −118.29 (m, 2F, $^3J_{PtF}$ = 327 Hz, *o*-Ar**F**), −161.86 (m, 1F, *p*-Ar**F**), −163.55 (m, 2F, $^4J_{PtF}$ = 114 Hz, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 65.34 (m, $^1J_{PtP}$ = 2295 Hz, P *trans* to C$_6$F$_5$), 59.92 (s, $^1J_{PtP}$ = 3720 Hz, P *cis* to C$_6$F$_5$) ppm. Anal. Calcd. for $C_{32}H_{48}ClF_5P_2Pt.0.5CH_2Cl_2$: %C, 45.24; %H, 5.74. Found: %C, 44.81; %H, 5.72. X-Ray diffraction quality crystals grown from CH$_2$Cl$_2$/hexane.

[1,2-bis(dimethylamino)ethane](iodo)(pentafluorophenyl)palladium(II) 6a. To a solution of **5** (200 mg, 0.35 mmol) in benzene (10 mL) was added iodopentafluorobenzene (51 mL, 0.38 mmol) and tmeda (58 mL, 0.38 mmol) and the reaction mixture was heated at reflux for 2 h. The solution was cooled and filtered through Celite. The solvent was removed *in vacuo* and the residue extracted with hot hexanes until no color persisted in the washings. The product was recrystallized from CH$_2$Cl$_2$/hexane to afford the product as a pale orange powder (154 mg, 86%). ^{1}H NMR (CDCl$_3$): δ 2.88 (s, 6H, NC**H**$_3$), 2.74 (m, 4H, NC**H**$_2$), 2.54 (s, 6H, NC**H**$_3$) ppm. ^{19}F NMR (CDCl$_3$): δ −118.21 (m, 2F, *o*-Ar**F**), −160.34 (m, 1F, *p*-Ar**F**), −163.47 (m, 2F, *m*-Ar**F**) ppm. Anal. Calcd. for $C_{12}H_{16}F_5IN_2Pd$: %C, 27.90; %H, 3.13. Found: %C, 27.98; %H, 2.95.

[1,2-bis(2,6-dimethylphenylimino)ethane](iodo)(pentafluorophenyl)palladium(II) 6b. To a solution of **5** (200 mg, 0.35 mmol) in benzene (10 mL) was added dmpe (101 mg, 0.38 mmol) and iodopentafluorobenzene (51 µL, 0.38 mmol). The reaction mixture was heated at reflux for 2 h. The solution was filtered through Celite and the solvent was removed *in vacuo*. The residue was extracted with hot hexanes until no color persisted in the washings. Recrystallization from CH$_2$Cl$_2$/hexane afforded the product as an orange microcrystalline powder (204 mg, 86%). ^{1}H NMR (CDCl$_3$): δ 8.27 (s, 1H, N=C**H**), 8.17 (s, 1H, N=C**H**), 7.21 (m, 4H, *m*-Ar**H**), 7.05 (m, 1H, *p*-Ar**H**), 6.96 (m, 1H, *p*-Ar**H**), 2.41 (s, 6H, o-ArC**H**$_3$), 2.29 (s, 6H, o-ArC**H**$_3$) ppm. ^{19}F NMR (CDCl$_3$): δ −115.80 (m, 2F, *o*-Ar**F**), −160.81 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-Ar**F**), −164.14 (m, 2F, *m*-Ar**F**) ppm. Anal. Calcd. for $C_{24}H_{20}F_5IN_2Pd$: %C 43.36; %H 3.04. Found: %C 43.54; %H 3.01. X-Ray diffraction quality crystals were grown from CH$_2$Cl$_2$/hexane.

[1,2-bis(dimethylphosphino)ethane](iodo)(pentafluorophenyl)palladium(II) 6c. To a suspension of **5** (200 mg, 0.35 mmol) in benzene (10 mL) was added a solution of dmpe (64 µL, 0.38 mmol) and iodopentafluorobenzene (51 µL, 0.38 mmol) in benzene. The reaction mixture was heated at reflux for 2 h. The solution was cooled and filtered through Celite. The solvent of the filtrate was removed *in vacuo*, and the residue was extracted with hot hexanes until no color persisted. The resulting pale yellow powder was recrystallized from CH$_2$Cl$_2$/hexane to afford the product as a pale yellow microcrystalline powder (103 mg, 54%). ^{1}H NMR (CDCl$_3$): δ 2.07–1.86 (m, 4H, PC**H**$_2$), 1.85 (d, 6H, $^2J_{PH}$ = 10 Hz, PC**H**$_3$), 1.48 (d, 6H, $^2J_{PH}$ = 11 Hz, PC**H**$_3$) ppm. ^{19}F NMR (CDCl$_3$): δ −115.93 (m, 2F, *o*-Ar**F**), −160.15 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-Ar**F**), −162.80 (m, 2F, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 46.93 (m, P *trans* to I), 38.74 (m, P *trans* to C$_6$F$_5$) ppm. Anal. Calcd. for $C_{12}H_{16}F_5IP_2Pd$: %C, 26.12; %H, 2.94. Found: %C, 25.93; %H, 2.81.

Aqua[1,2-bis(dimethylphosphino)ethane](pentafluorophenyl)platinum(II) triflate 7a. A suspension of **4c** (100 mg, 0.18 mmol) in chloroform (10 mL) was added to a suspension of AgO$_3$SCF$_3$ (47 mg, 0.18 mmol) in chloroform (5 mL). The reaction mixture was stirred at room temperature for 4 h. The solution was filtered through Celite, and the volume of the supernatant was reduced *in vacuo* to 5 mL. Toluene (10 mL) was added and the remaining chloroform was removed *in vacuo*. The resulting white crystalline powder was obtained by filtration (67 mg, 54%). ^{1}H NMR (CDCl$_3$): δ 2.86 (ds, 2H, H$_2$O), 2.45–2.12 (m, 4H, PC**H**$_2$), 1.87 (d, 6H, $^2J_{PH}$ = 11 Hz, $^3J_{PtH}$ = 20 Hz, PC**H**$_3$), 1.79 (d, 6H, $^2J_{PH}$ = 13 Hz, $^3J_{PtH}$ = 53 Hz, PC**H**$_3$) ppm. ^{19}F NMR (CDCl$_3$): δ −79.21 (s, 3F, SO$_3$CF$_3$), −119.63 (m, 2F, $^3J_{PtF}$ = 262 Hz, o-Ar**F**), −161.73 (bs,1F, *p*-Ar**F**), −164.34 (bs, 2F, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 40.27 (m, $^1J_{PtP}$ = 2374 Hz, P *trans* to C$_6$F$_5$), 19.69 (s, $^1J_{PtP}$ = 3842 Hz, P *cis* to C$_6$F$_5$) ppm. Anal. Calcd. for $C_{13}H_{18}F_8O_4P_2PtS$: %C, 22.98; %H, 2.68. Found: %C, 22.38; %H, 2.56. X-ray diffraction quality crystals were grown from CH$_2$Cl$_2$/hexane.

Aqua[1,2-bis(dicyclohexylphosphino)ethane](pentafluorophenyl)platinum(II) triflate 7b. To a suspension of AgOTf (32 mg, 0.13 mmol) in CHCl$_3$ (5 mL) was added a solution of **4d** (100 mg, 0.13 mmol) in CHCl$_3$ (5 mL) dropwise at room temperature. The reaction mixture was stirred at room temperature for 4 h. The solution was filtered through Celite and the volume of the solvent was reduced to 5 mL *in vacuo*. Hexane was added and the solvent reduced in volume *in vacuo* until crystallization was complete. Filtration afforded the product as a white crystalline powder (100 mg, 82%). ^{1}H NMR (CDCl$_3$): δ 2.42–2.22 (m, 4H, PC**H**$_2$ and C**H**$_2$ from C$_6$H$_{11}$), 2.22 (bs, 2H, O**H**$_2$), 2.10–1.12 (m, 42H, PC$_6$H$_{11}$), 0.85–0.78 (m, 2H, PC**H**$_2$) ppm. ^{19}F NMR (CDCl$_3$): δ −78.21 (s, 3F, SO$_3$C**F**$_3$), −119.12 (m, 2F, $^3J_{PtF}$ = 264 Hz, *o*-Ar**F**), −159.27 (m, 1F, *p*-Ar**F**), −163.23 (m, 2F, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 71.30 (m, $^1J_{PtP}$ = 2332 Hz, P *trans* to C$_6$F$_5$), 53.63 (s, $^1J_{PtP}$ = 4298 Hz, P *cis* to C$_6$F$_5$) ppm. Anal. calcd. for $C_{33}H_{50}F_8O_4P_2PtS.CH_2Cl_2$: %C, 39.38; %H, 5.06. Found: %C, 38.92; %H, 4.80.

[1,2-bis(dimethylphosphino)ethane]bis(pentafluorophenyl)palladium(II) 8. *Method 1*. To a suspension of AgOTf (56 mg, 0.22 mmol) in CHCl$_3$ (10 mL) was added a suspension of **3c** (100 mg, 0.22 mmol) in CHCl$_3$ (10 mL) dropwise with stirring. After the addition was complete, the reaction mixture was stirred at room temperature for 2 h. The solution was filtered through Celite and the solvent reduced in volume *in vacuo* to 5 mL. Toluene (10 mL) was added and the solvent reduced in volume *in vacuo* until precipitation was complete. Filtration afforded the product as a white powder (48 mg, 76%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.95 (m, 4H, PC**H**$_2$), 1.43 (d, 12H, $^2J_{PH}$ = 10 Hz, PC**H**$_3$) ppm. ^{19}F NMR (CD$_2$Cl$_2$): δ −115.61 (m, 4F, *o*-Ar**F**), −162.52 (t, 2F, $^3J_{FF}$ = 19 Hz, *p*-Ar**F**), −164.26 (m, 4F, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 36.31 (m) ppm. Anal. Calcd. for $C_{18}H_{16}F_{10}P_2Pd$: %C, 36.60; %H, 2.34. Found: %C, 36.27; %H, 2.75.

Method 2. To a solution of [Pd(C_6F_5)$_2$(tht)$_2$] **1a** (100 mg, 0.16 mmol) in THF (5 mL) was added a solution of dmpe (28 µL, 0.17 mmol) in THF (5 mL) and the reaction was stirred at room temperature for 4 h. The solvent was removed *in vacuo*. The residue was recrystallized from CH_2Cl_2/hexanes to afford the product as a white powder (84 mg, 88%).

[1,2-bis(dimethylphosphino)ethane]bis(pentafluorophenyl)-platinum(II) 10. *Method 1*. To a suspension of AgOTf (25 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was added a solution of **4c** (50 mg, 0.1 mmol) in $CHCl_3$ (10 mL), and the reaction mixture was stirred at room temperature for 2 h. The solution was filtered through Celite. The resulting solution was then stirred at room temperature for 3 weeks. The solution was filtered and the solvent removed *in vacuo*. Recrystallization from CH_2Cl_2/hexane afforded the product as a colorless crystalline solid (22 mg, 61%). ^{1}H NMR ($CDCl_3$): δ 1.94–1.80 (m, 4H, PC**H**$_2$), 1.54 (d, 12H, $^2J_{PH}$ = 10 Hz, $^3J_{PtH}$ = 28 Hz, PC**H**$_3$) ppm. ^{19}F NMR ($CDCl_3$): δ −118.18 (m, 4F, $^3J_{PtF}$ = 332 Hz, *o*-Ar**F**), −162.02 (m, 2F, *p*-Ar**F**), −163.83 (m, 4F, $^4J_{PtF}$ = 70 Hz, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.33 (bm, $^1J_{PtP}$ = 2246 Hz) ppm. Anal. Calcd. for $C_{18}H_{16}F_{10}P_2Pt$: %C, 31.82; %H, 2.38. Found: %C, 31.72; %H, 2.37.

Method 2. To a solution of [Pt(C_6F_5)$_2$(tht)$_2$] **2a** (75 mg, 0.11 mmol) in THF (5 mL) was added a solution of dmpe (20 µL, 0.12 mmol) in THF (5 mL) and the reaction mixture was stirred for 4 h at room temperature. The solvent was removed *in vacuo*. The residue was recrystallized from CH_2Cl_2/hexanes to give the product as a white powder (55 mg, 76%).

Bis[1,2-bis(dicyclohexylphosphino)ethane]palladium(II) triflate 9. To a suspension of AgOTf (35 mg, 0.14 mmol) in $CHCl_3$ (10 mL) was added a solution of **3d** (100 mg, 0.14 mmol) in $CHCl_3$ (10 mL) dropwise. The reaction mixture was stirred at room temperature for 2 h, after which time the solution was filtered through Celite. Toluene (10 mL) was added and the solution was reduced in volume *in vacuo* until precipitation was complete. Filtration afforded the product as a white powder (74 mg, 80%). ^{1}H NMR (CD_2Cl_2): δ 2.40–2.04 (m, 12 H, 2 × PC**H**$_2$ and 2 × C**H**$_2$ from C_6H_{11}), 2.00–1.68 (m, 18H, C_6**H**$_{11}$), 1.56–1.18 (m, 22H, C_6**H**$_{11}$) ppm. ^{19}F NMR (CD_2Cl_2): δ −78.94 (s, 3F, C**F**$_3$SO$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 106.71 (bs) ppm. Anal. Calcd. for $C_{54}H_{96}F_6O_6P_4PdS_2\cdot 4CHCl_3$: %C, 40.32; %H, 5.79. Found: %C, 39.94; %H, 6.11.

[1,2-bis(dimethylphosphino)ethane](hydrido)(pentafluorophenyl)platinum(II) 11a. To a suspension of **4c** (150 mg, 0.27 mmol) in THF (10 mL) was added $NaBH_4$ (12 mg, 0.32 mmol) and the reaction mixture was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was extracted with ether. The solvent of the combined extracts was removed *in vacuo* to afford the product as an off-white crystalline powder (83 mg, 59%). ^{1}H NMR (C_6D_6): δ 1.02 (d, 6H, $^2J_{PH}$ = 10 Hz, $^3J_{PtH}$ = 34 Hz, PC**H**$_3$), 0.88 (dd, 6H, $^2J_{PH}$ = 9 Hz, $^4J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 20 Hz, PC**H**$_3$), 0.81–0.58 (m, 4H, PC**H**$_2$), −1.48 (ddm, 1H, $^2J_{P(trans)H}$ = 200 Hz, $^2J_{P(cis)H}$ = 17 Hz, $^1J_{PtH}$ = 1080 Hz, Pt**H**) ppm. ^{19}F NMR (C_6D_6): δ −113.77 (m, 2F, $^3J_{PtF}$ = 402 Hz, *o*-Ar**F**), −163.72 (m, 1F, *p*-Ar**F**), −164.81 (m, 2F, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 30.46 (s, $^1J_{PtP}$ = 1616 Hz, P *trans* to H), 24.27 (m, $^1J_{PtP}$ = 2362 Hz, P *trans* to C_6F_5) ppm. Anal. Calcd. for $C_{12}H_{17}F_5P_2Pt$: %C, 28.08; %H, 3.34. Found: %C, 27.88; %H, 2.91.

[1,2-bis(dicyclohexylphosphino)ethane](hydrido)(pentafluorophenyl)platinum(II) 11b. To a solution of **4d** (100 mg, 0.12 mmol) in THF (10 mL) was added [Cp_2ZrH_2] (36 mg, 0.12 mmol) and the reaction mixture was stirred at room temperature for 10 h. The solvent was removed *in vacuo* and the residue extracted with benzene. The solution was filtered through Celite. The solvent was removed *in vacuo* to afford the product as a white microcrystalline powder. ^{1}H NMR (benzene-d_6): δ 2.2–0.8 (m, 48H, C_6**H**$_{11}$ and PC**H**$_2$), −0.30 (ddm, 1H, $^2J_{P(cis)H}$ = 4.5 Hz, $^2J_{P(trans)H}$ = 165 Hz, $^1J_{PtH}$ = 1036 Hz, Pt**H**) ppm. ^{19}F NMR (benzene-d_6): δ −114.98 (m, 2F, $^2J_{PtF}$ = 400 Hz, *o*-Ar**F**), −164.50 (m, 1F, *p*-Ar**F**), −165.30 (m, 2F, $^4J_{PtF}$ = 41 Hz, *m*-Ar**F**) ppm. ^{31}P{^{1}H} NMR (benzene-d_6): δ 74.45 (sept, J = 8.5 Hz, $^1J_{PtP}$ = 2482 Hz, P *trans* to C_6F_5), 65.50 (s, $^1J_{PtP}$ = 1777 Hz, P *cis* to C_6F_5) ppm. Anal. Calcd. for $C_{32}H_{49}F_5P_2Pt$: %C, 48.90; %H, 6.30. Found: %C, 48.71; %H, 5.96.

Crystallographic structural determinations. Diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer. Crystal, data collection, and refinement parameters are given in Table 1. The space groups were chosen based on the systematic absences (**4c**, **4d**), systematic absences and intensity statistics (**3a**, **4a**, **8**), and intensity statistics (**6b**, **7a**, **11b**). The structures were solved using the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. SADABS absorption corrections were applied to all data, except **7a** (T_{min}/T_{max} = 0.280) where absorption correction was done by DIFABS. In the crystal structure of **4d**, the highly disordered CH_2Cl_2 solvate molecule was treated by SQUEEZE.[22] Corrections of the X-ray data by SQUEEZE (187 electron/cell) were close to the required value (168 electron/cell for one CH_2Cl_2 molecule in a general position). All non-hydrogen atoms were refined with anisotropic displacement coefficients, except the C(7) and C(8) carbon atoms in **3a** and **4a** (disordered over two positions in ratio 45/55) and the C, Cl atoms of CH_2Cl_2 solvent molecule in **4c** (disordered around a center of symmetry), which were refined with isotropic thermal parameters. Hydrogen atoms were treated as idealized contributions, except all H atoms in **6b** and the H(1) atom in **11b**, which were found from the F-map and refined with isotropic thermal parameters, and the H atoms of water molecules in **7a** where the H atoms were not taken in consideration. The Flack parameters for **3a** and **4a** are 0.04(6) and 0.01(1), respectively. The b and c parameters and β and γ angles for the unit cell of **7a**, as well as the value of Z', suggest the possibility of higher symmetry, but none was found. The four independent molecules found in **7a** may be related to the asymmetrical arrangement of CF_3SO_3 groups in the crystal structure. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

CCDC reference numbers 227751–227758 for complexes **3a**, **4a**, **4c**, **4d**, **6b**, **7a**, **8**, and **11b**.

See http://www.rsc.org/suppdata/dt/b4/b406602b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

RPH is grateful to the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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