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Cyclopalladated complexes containing 2-C₆R₄PPh₂ ligands (R = H, F): one-electron electrochemical reduction leading to metal–carbon σ -bond cleavage *via* palladium(I)

Gopa Kar, Steven H. Privér, Lathe Jones, Si-Xuan Guo, Angel A. J. Torriero, Alan M. Bond, Martin A. Bennett and Suresh K. Bhargava*

Cyclopalladated complexes containing the 2-C₆F₄PPh₂ fragment have been prepared. The electrochemical reduction of these new complexes, as well as known structurally-similar species, were investigated using cyclic, rotating disk and microelectrode voltammetry.

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PAPER

Cyclopalladated complexes containing
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Gopa Kar,^a Steven H. Privér,^a Lathe Jones,^a Si-Xuan Guo,^b Angel A. J. Torriero,^{‡b}
Alan M. Bond,^b Martin A. Bennett^c and Suresh K. Bhargava^{*a}

Three new *ortho*-metallated palladium complexes, [Pd(O,O'-hfacac)(κ^2 -2-C₆F₄PPh₂)] (**11**), [Pd₂(O,O'-hfacac)₂(μ -2-C₆F₄PPh₂)₂] (**12**) and [Pd(O,O'-hfacac)(κ C-2-C₆F₄PPh₂)(PPh₃)] (**13**) (hfacac = hexafluoroacetate), have been prepared and fully characterised. The electrochemical reductions of complexes **11–13**, together with those of other cyclopalladated complexes containing 2-C₆R₄PPh₂ ligands (R = H, F) were studied by cyclic, rotating disk and microelectrode voltammetry. Evidence for the one-electron reduction of [Pd(κ^2 -2-C₆F₄PPh₂)(PPh₂)] (**6**) was obtained from coulometric analysis, although the product is unstable and undergoes further chemical processes. Preparative electro-reduction of [Pd₂(μ -Br)₂(κ^2 -2-C₆F₄PPh₂)₂] (**7**) in CH₂Cl₂ causes reductive cleavage of its Pd–C σ -bonds and formation of the complex [PdBr₂{PPh₂(2-C₆F₄H)}₂] (**14**); possible mechanisms are discussed.

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Introduction

Aryl carbanions of the type [2-C₆R₄PPh₂][−] (R = H, F) bind to transition metal centres in two principal ways: as bidentate, chelate ligands to one metal atom, $\kappa^2(P,C)$, forming a four-membered ring, and as bidentate, bridging ligands, $\mu_2(P,C)$, forming an eight-membered ring containing two metal atoms.¹ These modes are sometimes interconvertible through reversible dissociation of the M–P bond. For example, depending on the steric bulk of the auxiliary tertiary phosphine, planar palladium(II) complexes PdBr(2-C₆H₄PPh₂)(PR₃) are either mononuclear, containing κ^2 -2-C₆H₄PPh₂ (**I**), for PR₃ = PPh₃ or PCy₃, or dinuclear, containing μ_2 -2-C₆H₄PPh₂ (**II**), for PR₃ = PMe₃; for PR₃ = PMe₂Ph, both structures coexist in solution.^{2,3} In the case of palladium(II) with 2-C₆F₄PPh₂, two com-

plexes of the same composition, PdX(2-C₆F₄PPh₂) (X = Cl, Br), have been isolated: (**III**) is dinuclear with bridging halides and κ^2 -2-C₆F₄PPh₂,^{4,5} whereas (**IV**) is tetranuclear, with bridging halides and μ_2 -2-C₆F₄PPh₂;⁶ (**IV**) appears to be thermodynamically more stable.

Comproportionation of the bis(chelate) complex *trans*-[Pd^{II}-(κ^2 -2-C₆F₄PPh₂)₂]⁴ with [Pd⁰(PPh₃)₄] generates a dipalladium(I) complex [Pd^I₂(μ_2 -2-C₆F₄PPh₂)₂(PPh₃)₂] (**V**), in which the two bridging ligands adopt a head-to-tail arrangement⁷ (Scheme 1); **V** undergoes facile oxidative addition at the dimetal centre with halogens and with organic halides.

Scheme 1

^aCentre for Advanced Materials and Industrial Chemistry (CAMIC), School of Applied Sciences (Applied Chemistry), RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia

^bSchool of Chemistry, Monash University, Clayton, Victoria 3800, Australia

^cResearch School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

[†]Electronic supplementary information (ESI) available: Cyclic voltammograms in CH₂Cl₂ and CH₃CN for complexes **1–5**, **7** and **9** and X-ray crystallographic data in CIF format for complexes **11–14**. CCDC 1024463–1024466. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt03268c

[‡]Current address: Centre for Chemistry and Biotechnology, School of Life and Environmental Sciences, Deakin University, Burwood, Victoria 3125, Australia.

electro-oxidation of ferrocenyldiphenylphosphine (PPh_2Fc) complexes of type **I**,¹⁸ Lahuerta *et al.*⁶ have shown that, in the presence of chloride ion, $[\text{Pd}_2(\mu\text{-OAc})_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ undergoes one-electron electro-oxidation at each metal centre to the corresponding dipalladium(III) complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-OAc})_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ and Ubeda *et al.*¹⁹ have shown that β -diketonato- or phenolato-complexes, such as $[\text{Pd}_2(\text{O},\text{O}'\text{-acac})_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ (**3**), undergo similar irreversible, probably one-electron, electro-oxidation at each metal centre.

Synthesis and characterisation of new compounds

The dimeric analogue of **11**, $[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ (**12**) was prepared similarly by treating $[\text{Pd}_2(\text{O},\text{O}'\text{-acac})_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ ⁵ (**8**) with an excess of hexafluoroacetylacetone (Scheme 3). Complex **12** could also be formed by allowing a dichloromethane–methanol solution of **11** to stand at ambient temperature for two days; there was no evidence for the dimerisation of **11** in dichloromethane alone. The ¹H NMR spectrum of **12** is similar to that of **11** and only shows a single methine resonance at δ 6.13 due to the equivalent hfacac groups. The ³¹P NMR spectrum shows a multiplet at δ 25.8, the chemical shift being comparable to that of **8** (δ 24.5)⁵ and to the chemical shifts of the structurally similar complexes $[\text{Pd}_2(\text{O},\text{O}'\text{-acac})_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ (**3**) (δ 26.4) and $[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ (δ 26.9).¹⁹

In the crystal structure of $[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**12**), shown in Fig. 2, two palladium atoms are coordinated by two chelating hexafluoroacetylacetonate ligands and two bridging $2\text{-C}_6\text{F}_4\text{PPh}_2$ groups. The Pd...Pd separation in **12** [2.9345(6) Å]

Scheme 2

Fig. 1 Molecular structure of $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)]$ (**11**). Only one of the two independent molecules in the unit cell is shown. Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.2286(6), Pd(1)–C(1) 1.987(2), Pd(1)–O(1) 2.0782(16), Pd(1)–O(2) 2.0728(16), P(1)–Pd(1)–C(1) 69.97(7), O(1)–Pd(1)–O(2) 90.66(6), P(1)–Pd(1)–O(2) 101.22(5), C(1)–Pd(1)–O(1) 98.11(8), P(1)–Pd(1)–O(1) 168.05(5), C(1)–Pd(1)–O(2) 170.99(9).

Scheme 3

is significantly smaller than those in **8** [2.9640(3) Å], **3** [2.9762(5) Å] and $[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ [2.9891(1) Å]⁵ and may indicate a weak metal–metal interaction. The bond lengths and angles in **12** are generally comparable to those in **8**, although the Pd–O bond lengths are slightly longer (*ca.* 2.08–2.09 Å vs. 2.06 Å), consistent with the greater lability of the hexafluoroacetylacetonate ligand compared to its protio analogue.

The *P,C* chelate ring in $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)]$ (**11**) was opened by the addition of a stoichiometric amount of triphenylphosphine to give $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa\text{-2-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_3)]$ (**13**) (Scheme 2), which was isolated almost quantitatively as a yellow solid. The ³¹P NMR spectrum of **13** showed two broad unresolved multiplets at δ –30.2 and +28.2, corresponding to the phosphorus nuclei in the $\text{C}_6\text{F}_4\text{PPh}_2$ and PPh_3 ligands, respectively. The ¹⁹F NMR spectrum showed the expected four peaks assignable to the $\text{C}_6\text{F}_4\text{PPh}_2$ ligand and a single broad resonance at δ –75.5 due to overlap of the two CF_3 groups of hfacac. Presumably the broadness of the resonances in the ¹⁹F and ³¹P NMR spectra is due to rapid intermolecular exchange arising from reversible dissociation of the PPh_3 and re-association of the phosphorus atom of $\text{C}_6\text{F}_4\text{PPh}_2$.

Fig. 2 Molecular structure of $[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ (**12**). Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity. The crystals were twinned due to the monoclinic angle being close to 90° [twin law: 1 0 0 –1 0 0 –1; 0.4281(7) twin contribution]. The trifluoromethyl groups at C(41) and C(46) displayed rotational disorder of 72 and 56%, respectively. Selected bond lengths (Å) and angles (°): Pd(1)–Pd(2) 2.9345(6), Pd(1)–P(2) 2.2379(12), Pd(2)–P(1) 2.2543(12), Pd(1)–C(1) 1.978(4), Pd(2)–C(19) 1.991(4), Pd(1)–O(1) 2.102(3), Pd(1)–O(2) 2.076(3), Pd(2)–O(3) 2.083(3), Pd(2)–O(4) 2.081(3), P(2)–Pd(1)–C(1) 87.80(12), O(1)–Pd(1)–O(2) 89.31(12), P(2)–Pd(1)–O(2) 95.24(9), C(1)–Pd(1)–O(1) 87.42(14), P(2)–Pd(1)–O(1) 171.67(10), C(1)–Pd(1)–O(2) 176.33(14).

Fig. 3 Molecular structure of $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa\text{-2-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_3)]$ (**13**). Ellipsoids show 50% probability levels. Hydrogen atoms and solvents of crystallisation have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(2) 2.2310(7), Pd(1)–C(1) 1.984(2), Pd(1)–O(1) 2.1140(18), Pd(1)–O(2) 2.0967(18), P(2)–Pd(1)–C(1) 91.79(7), O(1)–Pd(1)–O(2) 89.25(7), P(2)–Pd(1)–O(2) 90.51(5), C(1)–Pd(1)–O(1) 88.43(9), P(2)–Pd(1)–O(1) 178.67(5), C(1)–Pd(1)–O(2) 177.57(9).

The presence of the dangling PPh_2 group in **13** was confirmed by single-crystal X-ray diffraction and the molecular structure is shown in Fig. 3.

The Pd–C and Pd–P bond lengths in **13** are similar to those in **11**, while the Pd–O bond lengths are *ca.* 0.03 Å longer. The phosphorus atom of the 2-C₆F₄PPh₂ group is located above the palladium atom to give a pseudo-square pyramidal arrangement about the metal atom, although the Pd⋯P distance of *ca.* 3.1 Å indicates the absence of a formal bond.

Electrochemical behaviour of the palladium complexes

All potentials in this report are quoted relative to the DmFc^{0/+} potential scale, where DmFc is decamethylferrocene. The supporting electrolyte in all cases was 0.1 M [*n*-Bu₄N][PF₆]. In cyclic voltammetry, peak potential and peak current data provided in the text below for the irreversible reduction processes refer to a scan rate of 100 mV s^{−1}, unless otherwise stated. Peak currents for major processes were proportional to the square root of the scan rate over the range of 50 to 1000 mV s^{−1} and reduction peak potentials became slightly more negative with increasing scan rate over the same range.

[PdBr(L)(κ²-2-C₆H₄PPh₂)] [L = PPh₃ (**1**), PPh₂Fc (**2**)] and [Pd₂(O,*O'*-acac)₂(μ-2-C₆H₄PPh₂)₂] (**3**)

Cyclic voltammograms of **1** in CH₃CN (Fig. S1†) exhibited an irreversible reduction process which probably occurs, at least initially, at the metal centre with a fairly negative peak potential (*E*_{red}^p) of −1.96 V. It is difficult to estimate the number of electrons transferred (*n*-value) for irreversible processes under conditions of transient voltammetry. Sometimes this can be achieved by analysis of steady state limiting currents (*i*_L) obtained by rotating disk electrode (RDE) or microelectrode voltammetry for both reversible and many classes of irreversible process under mass transport controlled conditions where the magnitude of the limiting current is a function of *n* (and other parameters like electrode area or radius and the diffusion coefficient). Unlike transient peak currents (*E*^p values), *i*_L is independent of electrode kinetics and *i*R (ohmic) drop. In this case, because RDE and microelectrode experiments for **1** failed to give potential-independent steady-state plateau currents, the number of electrons transferred in this reduction process could not be determined. Nevertheless, since the current magnitude per unit is much larger than for reversible one-electron oxidation processes described below, it is assumed that this is a multi-electron reduction process.

While the *n*-value is unknown for **1**, loss of halide could be detected on the reverse oxidative scan in cyclic voltammograms. One small process was observed at a potential of about +0.60 V, which is assigned to the electro-oxidation of Br[−] that had been released during electro-reduction.²¹

The cyclic voltammogram for complex **2** in CH₂Cl₂ (Fig. S2a†) showed a well-defined redox couple with a mid-point potential (*E*^m) at *ca.* +0.70 V that was electrochemically reversible on the voltammetric time-scale and is readily assigned to the one-electron (PPh₂Fc)^{0/+} oxidation. This ferrocene-based oxidation process has been studied in detail and the diffusion coefficient established (6.4 × 10^{−6} cm² s^{−1} in CH₂Cl₂ and 7.9 × 10^{−6} cm² s^{−1} in CH₃CN).¹⁸ The magnitude of

the current per unit concentration for this process therefore provides a reference point for the value predicted for an *n* = 1 reduction process under transient and steady-state conditions. At both room temperature and −25 °C there was a reduction process with a much larger current at *ca.* −1.80 V, which was irreversible on the cyclic voltammetric time-scale and whose reductive limiting current, according to RDE experiments, was about 3.7 times that of the oxidation current of the ferrocene centre where *n* = 1.0. Coulometric analysis of the current-time plot of controlled potential bulk electrolysis at a potential of −1.95 V also indicated the number of electrons to be close to four. Thus, having been generated at a very negative potential, the initial reduction product, which is presumably Pd(I), is highly reactive and evidently undergoes additional coupled chemical and electron-transfer processes.

In CH₃CN (Fig. S2b†), the one-electron oxidation of PPh₂Fc in complex **2** appeared at a similar potential to that in CH₂Cl₂ but the reduction peak now had a shoulder, its *E*_{red}^p had shifted to −1.63 V and the magnitude of the peak current was now almost equal to that of the ferrocene centre. Thus, the overall reduction of **2** is close to a one-electron process in CH₃CN but a multi-electron process in CH₂Cl₂. Unfortunately, for this process, a potential-independent limiting current could not be obtained at a RDE in CH₃CN in order to verify an overall value of *n* = 1.

The marked solvent shift in *E*_{red}^p of 0.17 V is attributed to the predominance in CH₃CN of the *cis*-isomer of **2**,¹⁸ which is probably more easily reduced than the *trans*-isomer. In support of this proposal, *E*_{red}^p for the two-electron reduction of *cis*-[PtCl₂(PPh₃)₂] in CH₃CN–C₆H₆ is *ca.* 0.2 V less negative than that for the corresponding *trans*-isomer, probably reflecting a lower electron density at the metal centre in the *cis*-isomer.²² A similar trend is evident in the potentials for the reductions of *cis*- and *trans*-[Pd(NO₂)₂(NH₃)₂] in an aqueous medium.²³ It may also be that the reduction product is stabilised by CH₃CN coordination.

Complex **3** in CH₃CN showed an irreversible reduction process at the very negative potential of −2.11 V but further studies have not been carried out owing to the proximity to the solvent limit and the poor solubility of the compound.

[PdX(L)(κ²-2-C₆F₄PPh₂)] [X = Br, L = PPh₃ (**4**), PPh₂Fc (**5**); X = I, L = PPh₂Fc (**6**)]

The bromo-complexes **4** and **5** (1.0 mM) in CH₂Cl₂ (Fig. S3 and S4,† respectively) showed irreversible reduction processes with *E*_{red}^p values of −1.44 and −1.56 V, respectively, *i.e.*, *ca.* 0.4 V more positive than **2**, reflecting the easier reducibility of the metal centre resulting from replacement of 2-C₆H₄PPh₂ by the more electron-withdrawing 2-C₆F₄PPh₂.

The iodo-complex **6** (5.0 mM) in CH₂Cl₂ and CH₃CN showed, in each case, an irreversible reduction with *E*_{red}^p at −1.37 V and −1.23 V, respectively (Fig. 4a). In addition, both **5** and **6** displayed the expected reversible one electron oxidation process arising from the ferrocene centres at potentials of +0.72 and +0.74 V, respectively. In both cases, the reduction peak current magnitude was almost equal to that of the *n* = 1.0

Fig. 4 (a) Cyclic voltammogram of 5 mM $[\text{Pd}(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_2\text{Fc})]$ (**6**) in CH_2Cl_2 obtained at a GC electrode (3 mm diameter). (b) Rotating disk voltammogram (1 mM) obtained at a GC electrode (3 mm diameter). Rotation rate: 1000 rpm; scan rate: 20 mV s^{-1} .

reference oxidation reaction at the ferrocene centre. RDE studies (Fig. 4b) confirmed that this was also true for the steady state currents for the two processes. Thus, for **5** and **6** in CH_2Cl_2 , and **2**, **5** and **6** in CH_3CN , the evidence clearly indicates that the main reduction is an irreversible one-electron process at the palladium atom.

On the reverse scan for **4** in CH_2Cl_2 , two small processes observed at positive potentials are probably due to the oxidation of Br^- that had been released in the reduction. Similar processes were not observed in the reverse oxidative potential direction scan of **5**, possibly because of overlap with the reversible $\text{PPh}_2\text{Fc}^{0/+}$ process, but in the case of **6**, a peak was observed at +0.38 V which can be assigned to the oxidation of I^- released during reduction (same process observed for the oxidation of I^- from $[n\text{-Bu}_4\text{N}]\text{I}$).

When the potentials of **4** and **5** in CH_2Cl_2 were scanned in the very negative potential region close to the solvent limit, small reduction processes were also observed at ca. -1.77 V, while for **6**, two such processes were seen at -1.59 and -1.76 V. Since the cyclic voltammogram of $2\text{-BrC}_6\text{F}_4\text{PPh}_2$ also showed a reduction peak at ca. -1.77 V, these processes at more negative potentials may arise from addition of electrons to the fluorinated aromatic ring.

Fig. 5 (a) UV-Visible spectra of 0.07 mM $[\text{Pd}(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_2\text{Fc})]$ (**6**) in CH_2Cl_2 obtained from a spectroelectrochemical experiment over the course of reductive electrolysis at -1.45 V vs. $\text{DmFc}^{0/+}$. (b) Comparison of spectra obtained before (—) and after (—) electrolysis.

Coulometric analysis of a bulk electrochemical reduction of **6** in CH_2Cl_2 , at a controlled potential of -1.45 V at room temperature, gave an n -value of 1.1 ± 0.1 per molecule, consistent with reduction of $\text{Pd}(\text{II})$ to $\text{Pd}(\text{I})$. An *in situ* spectroelectrochemical study of the electro-reduction of a 0.07 mM solution of **6** in CH_2Cl_2 under the same conditions (Fig. 5a) showed a steady decrease in the intensity of the initially present absorption bands at 290 and 375 nm and the concomitant appearance of a new, weak band at ca. 450 nm (Fig. 5b). At first sight, this appeared to be consistent with the formation of a dipalladium(I) species, since the UV-Vis spectra of the dipalladium(I) complexes $[\text{Pd}_2(\text{dppf})_2(\text{CNR})_2][\text{PF}_6]_2$ ($\text{R} = 2,6\text{-xylyl}$, mesityl) are reported to show a band at 449 nm, possibly due to a $\sigma \rightarrow \sigma^*$ transition of the Pd-Pd bond.²⁴ However, all attempts to isolate, characterise, or even detect by ^{31}P NMR spectroscopy, the expected dipalladium(I) complex $[\text{Pd}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2(\text{PPh}_2\text{Fc})_2]$ [analogous to the PPh_3 complex (**V**) shown in Scheme 1] failed.

Bulk electrolysis of complex **4** in either CH_2Cl_2 or THF at room temperature with an applied potential of -1.5 V caused a colour change from yellow to dark orange. The ^{31}P NMR spectrum of the THF solution consisted of a series of resonances in the range δ 19–27, together with the expected septet due to

[PF₆][−]. Also present were a triplet and a doublet assignable to [PO₂F₂][−] and [PO₃F]^{2−}, respectively, arising from induced hydrolysis of the anion, presumably by small amounts of water in the solvent. The characteristic pair of peaks that would have been expected for [Pd₂(μ-2-C₆F₄PPh₂)₂(PPh₂Fc)₂] were not observed (for the PPh₃ analogue **V**, the chemical shifts are δ 8 and −19). Similar observations were made for the reduction in CH₂Cl₂, in which **4** is more soluble, except that the final ³¹P NMR spectrum now consisted of numerous overlapping multiplets in the range δ 10–40. The reduced solutions in both solvents darkened on standing indicating that the initially formed products were unstable and we did not attempt to isolate them.

[Pd₂(μ-Br)₂(κ²-2-C₆F₄PPh₂)₂] (**7**)

Cyclic voltammetry of a 1.0 mM solution of **7** in CH₂Cl₂ (Fig. S5†) showed two irreversible reduction processes with *E*_{red}^p at −0.95 and −1.65 V, the peak current of the second process being almost twice that of the first. The RDE results gave just one well-defined process at the less negative potential; application of the Levich equation²⁵ showed that two electrons per molecule were transferred, corresponding to a one-electron reduction (Pd^{II} → Pd^I) of both metal centres, and a diffusion coefficient of 6.6 × 10^{−6} cm² s^{−1} was obtained. The second reduction did not yield steady-state current plateaus in the RDE experiments because of its closeness to the solvent limit, and the *n*-value associated with this process cannot be specified. The reverse positive potential scan after switching of the potential after both reduction processes showed two small shoulders at +0.58 and +0.91 V attributable to the oxidation of Br[−] released during electro-reduction.²¹

It is noteworthy that the potential for the first reduction step in **7** is considerably less negative than that for complexes **1**, **2**, **4** and **6**, presumably as a consequence of the absence of the electron-donating tertiary phosphines PPh₃ or PPh₂Fc from the coordination sphere.

Bulk electrolysis of complex **7** in CH₂Cl₂ at ambient temperature and an applied potential of −1.3 V caused a colour change from yellow to orange. At the end of the electrolysis, the electrode was coated with a black layer, presumably metallic palladium. The ³¹P NMR spectrum (CH₂Cl₂–C₆D₆) of an aliquot of the solution after reduction showed four resonances at δ 16.2 (major product), 17.7, 23.6 and 63.8, in addition to the expected septet at δ −144.5 due to the supporting electrolyte; also present was a low intensity triplet at δ −18.6 due to [PO₂F₂][−]. After treatment of the crude solution with LiBr in methanol, the resonance at δ 17.7 was no longer present in the ³¹P NMR spectrum, suggesting that the species responsible for this peak may be a chloride-containing complex, presumably derived by reaction of an electrolytically reduced palladium species with the CH₂Cl₂ solvent. Purification of this mixture gave a yellow/orange solid, the ³¹P NMR spectrum of which only showed two resonances in approximately 11:1 ratio in the region δ 16–30. Single crystal X-ray diffraction (Fig. 6) showed one of these species to be *trans*-[PdBr₂{PPh₂(2-C₆F₄H)}₂] (**14**). The metrical parameters of **14** are unexcep-

Fig. 6 Molecular structure of *trans*-[PdBr₂{PPh₂(2-C₆F₄H)}₂] (**14**). Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity. Asterisks indicate atoms generated by symmetry (−*x*, *y*, −*z* + 1/2). Selected bond lengths (Å) and angles (°): Pd(1)–P(2) 2.3248(8), Pd(1)–Br(1) 2.4300(5), P(1)–Pd(1)–Br(1) 93.34(2), P(1)–Pd(1)–Br(1*) 86.28(2), P(1)–Pd(1)–P(1*) 167.81(3), Br(1)–Pd(1)–Br(1*) 176.471(19).

tional and similar to those in *trans*-[PdBr₂(PPh₃)₂].²⁶ We tentatively assign the more intense resonance at δ 16.2 in the ³¹P NMR spectrum of the electro-reduced solution of **7** to *trans*-[PdBr₂{PPh₂(2-C₆F₄H)}₂] (**14**) and the less intense peak at δ 23.6 to the corresponding *cis*-isomer.

Independent identification of **14** was obtained by cleavage of the Pd–C σ-bonds in the bis(chelate) complex *trans*-[Pd(κ²-2-C₆F₄PPh₂)₂]⁴ with two equivalents of HBr (see Experimental). The ³¹P NMR spectrum of **14** in CH₂Cl₂–C₆D₆ prepared by this method showed a single resonance at δ 16.2. After the addition of a catalytic amount of [*n*-Bu₄N]Br, a new low intensity peak appeared at δ 23.9, the chemical shift of which is similar to that observed in the crude electro-reduced solution of **7**, reinforcing our suggestion that the species responsible for this resonance is *cis*-[PdBr₂{PPh₂(2-C₆F₄H)}₂]. Additional confirmation that the resonance at δ 17.7 in the ³¹P NMR spectrum of the electro-reduced solution was due to a chloride-containing species was obtained by mixing CH₂Cl₂–C₆D₆ solutions of *trans*-[PdCl₂{PPh₂(2-C₆F₄H)}₂] {prepared *in situ* from *trans*-[Pd(κ²-2-C₆F₄PPh₂)₂] and HCl; δ_{31P} 18.2} and *trans*-[PdBr₂{PPh₂(2-C₆F₄H)}₂] to give the mixed-halide species *trans*-[PdClBr{PPh₂(2-C₆F₄H)}₂] (δ_{31P} 17.7). The UV-Visible spectrum of **14** showed a broad, barely resolved absorption in the region of 400–450 nm in addition to two more intense bands at 312 and 362 nm, so the absorption clearly is not diagnostic of a Pd–Pd bond, at least in the present series of compounds. Indeed, the result suggests that the reduction products of **6** may also contain coordinated PPh₂(2-C₆F₄H).

[Pd₂Br₂(NCMe)₂(μ-2-C₆F₄PPh₂)₂] (**9**)

Since complex **9** resembles geometrically the desired dipalladium(i) reduction product **V** in containing a pair of head-to-tail bridging 2-C₆F₄PPh₂ groups, its voltammetric reductive behaviour was of particular interest. In fact, it is generally similar

to those of complexes 4–6 and 7. A 0.7 mM solution in CH_2Cl_2 (Fig. S6†) showed two irreversible reduction processes at -1.39 and -1.69 V, the peak current of the first process being almost twice that of the second. Assuming the diffusion coefficient of **9** to be similar to that of **7**, we tentatively assign the first process to a one-electron reduction of each metal atom on the basis of its current magnitude per unit concentration, while the second reduction may correspond to a $\text{Pd}^{\text{I}} \rightarrow \text{Pd}^0$ step for one of the metal atoms. On the reverse scan, an oxidation process was observed at $+0.59$ V, which may be assigned as above to Br^- oxidation.²¹

It is worth noting that **7** is rapidly converted into **9** in CH_3CN ⁵ and that coordination of CH_3CN causes the first reduction potential at the palladium centres to become *ca.* 0.4 V more negative, *i.e.*, the presence of CH_3CN in the coordination sphere disfavours reduction.

$[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)]$ (**11**), $[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ (**12**) and $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa\text{C-2-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_3)]$ (**13**)

The cyclic voltammogram for **11** in CH_3CN showed an irreversible reduction process at -1.37 V closely followed by a series of less well defined and smaller processes. Experiments with an ultramicroelectrode and RDE studies were carried out in an attempt to determine the number of electrons (n) involved. With the assumption that the diffusion coefficient of **11** is equal to that of **5**, n was found to lie between 1 and 2 for the first reduction process, but in the absence of fully potential-independent, mass transport controlled limiting currents, more precise conclusions could not be drawn.

In the case of **12** in CH_3CN , there were two well-defined and fully resolved reduction processes having approximately equal intensity at -1.67 and -2.21 V. The first occurs at a potential about 0.5 V less negative than the reduction process observed for the corresponding acac complex **3**, the effect again being as expected for a more electron-withdrawing ligand if reduction is occurring at the metal centres.

Fig. 7 Cyclic voltammogram of a 5 mM solution of $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa\text{C-2-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_3)]$ (**13**) in CH_3CN (3 mm diameter CG electrode; scan rate: 50 mV s^{-1}).

Fig. 8 Microelectrode voltammogram of a 5 mM solution of $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa\text{C-2-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_3)]$ (**13**) in CH_3CN (5 μm radius; scan rate: 50 mV s^{-1}). Positions of expected diffusion limited currents for $n = 1$ and $n = 2$ reductions are shown.

At a scan rate of 50 mV s^{-1} , complex **13** in CH_3CN showed an initial reduction process at -1.22 V followed by a series of smaller processes up to the solvent limit, presumably due to reduction of products resulting from the first reduction process (Fig. 7). Microelectrode studies showed a reasonably well-defined diffusion controlled limiting current for the first process significantly below the current predicted for $n = 2$ (Fig. 8), which again leads us to believe that an initial one-electron process takes place to give a very reactive $\text{Pd}(\text{I})$ species.

Conclusions

All the $\text{Pd}(\text{II})$ complexes of $2\text{-C}_6\text{R}_4\text{PPh}_2$ ($\text{R} = \text{H}, \text{F}$) examined undergo at least one major irreversible reduction process at a glassy carbon electrode under conditions of cyclic voltammetry in CH_2Cl_2 or CH_3CN at potentials in the range -0.95 to -2.2 V versus the $\text{DmFc}^{0/+}$ potential scale. The potentials depend strongly on the ligand environment, being less negative, corresponding to easier reduction, when more electron-withdrawing ligands are introduced into the coordination sphere, *i.e.*, hfacac in place of acac and $2\text{-C}_6\text{F}_4\text{PPh}_2$ in place of $2\text{-C}_6\text{H}_4\text{PPh}_2$. Electro-reduction of halide complexes generates free halide ion in some cases, as detected on reverse positive (oxidative) potential direction scans, indicating that the electro-reduction takes place at the metal centre with loss of halide. The irreversible electro-reduction is observed irrespective of the mode of coordination (chelating or bridging) of $2\text{-C}_6\text{R}_4\text{PPh}_2$ in the initial complex.

The first reduction process is often accompanied by additional irreversible processes at more negative potentials, which are sometimes close to the solvent limit. In the complexes $[\text{PdX}(\text{L})(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)]$ (**4–6**), in either CH_2Cl_2 or CH_3CN , the combined cyclic voltammetric, rotating disk electrode and spectroelectrochemical results are consistent with the proposition that the first irreversible reduction is a one-

electron process at the metal centre, probably corresponding on the voltammetric time-scale to the overall reaction:

Although the evidence is not so clear-cut for complexes **7** and **9**, the first irreversible reduction process in each case may be described on the voltammetric time-scale by the reactions:

The subsequent fate of these initially-formed palladium(I) species is generally unknown; rapid reactions appear to take place with the solvent that prevent the observation of the expected dinuclear complexes such as **V**. Only in the case of complex **7** have we been able to establish the nature of the isolated reduction product, *viz.* $[\text{PdX}_2\{\text{PPh}_2(2\text{-C}_6\text{F}_4\text{H})\}_2]$ ($\text{X} = \text{Cl}, \text{Br}$), which evidently arises by protonolysis of the metal–carbon σ -bonds of **7**. The net equation for the electro-reduction can be written:

We cannot exclude the possibility that the added hydrogen atoms are derived from adventitious water but it seems more likely that they are abstracted from the dichloromethane solvent by rapid reaction with the initially electrogenerated palladium(I) species (which could be either mononuclear or dinuclear) forming chlorocarbene:

The fact that the reduction product of **14** contains both bromide and chloride supports the involvement of CH_2Cl_2 in the reaction sequence. It seems plausible that the hydrogen atoms are transferred initially to the metal and that the Pd–H bonds then insert into the metal–carbon bonds of the $2\text{-C}_6\text{F}_4\text{PPh}_2$ rings, leading to a dipalladium(I) complex $[\text{Pd}_2\text{X}_2\{\text{PPh}_2(2\text{-C}_6\text{F}_4\text{H})\}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) which subsequently disproportionates to **14** and Pd metal. The generation of hydride in the controlled potential bulk reductive electrolysis of Pt(II) complexes has been reported, *e.g.* *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ in $\text{C}_6\text{H}_6\text{-CH}_3\text{CN}$ gives *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$, the hydride ligand in this case being derived from the $[\text{Bu}_4\text{N}]^+$ cation.²⁷

Experimental

General comments

Complexes **1–7**, **9** and **10** were prepared by literature methods.^{3,5,18,19} In the case of **3**, the reported method³ was modified slightly: the salt $[\text{Pd}_2(\text{THF})_4(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2][\text{BF}_4]_4$, generated *in situ* from $[\text{Pd}_2(\mu\text{-Br})_4(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_4]$ (250 mg, 0.14 mmol) and AgBF_4 (109 mg, 0.56 mmol) in $\text{CH}_2\text{Cl}_2\text{-THF}$ was treated with $[\text{Na}(\text{acac})]$ (68 mg, 0.56 mmol) and the mixture was stirred overnight. The product was isolated as reported in 80% yield (209 mg).

Solvents used for synthesis were dried by use of a standard column drying system and all other chemicals were commercially available and used as received. ^1H (300 MHz), ^{19}F (282 MHz) and ^{31}P (121 MHz) NMR spectra were acquired on a Bruker Avance 300 spectrometer in C_6D_6 , unless otherwise stated, and chemical shifts (δ) are given in ppm, internally referenced to residual solvent signals (^1H), internal CFCl_3 (^{19}F) or external 85% H_3PO_4 (^{31}P). Mass spectra were acquired on a Perkin Elmer Axion II APCI TOF mass spectrometer with a direct sample analysis (DSA) attachment (RMIT University) or Bruker Apex 3 FTICR mass spectrometer (Research School of Chemistry, Australian National University); elemental analyses were performed by the Microanalytical Unit at the same School.

Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of an isopentane solution (**11**), dichloromethane–methanol (**12**), benzene–hexane (**13**) or dichloromethane–hexane (**14**). X-ray diffraction data were collected on a D8 Bruker diffractometer with an APEX2 area detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a 1 μS microsource. Geometric and intensity data were collected using SMART software.²⁸ The data were processed using SAINT²⁹ and corrections for absorption were applied using SADABS.³⁰ The structures were solved using direct methods and refined with full-matrix least-squares methods on F^2 using the SHELX-TL package.³¹ Selected crystal data and details of data collection and structure refinement are listed in Table 1.

Electrochemistry

Dichloromethane (HPLC grade, Merck) was dried over basic alumina and acetonitrile (HPLC grade, Merck) distilled over CaH_2 before use. Acetone (Merck), decamethylferrocene (DmFc, Aldrich), tetrabutylammonium bromide (Aldrich), tetrabutylammonium iodide (Aldrich) and ferrocene (Fc, BDH) were used as supplied by the manufacturer. Tetrabutylammonium hexafluorophosphate was purchased from GFS and recrystallised twice from ethanol before use.³²

Electrochemical experiments were carried out in a standard three electrode arrangement with Model 100B (Bioanalytical Systems, West Lafayette, IN, USA) or CHI920C (CH Instruments, Texas, USA) electrochemical workstations. A platinum wire auxiliary electrode and a Ag/AgCl (CH_2Cl_2 , 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$) single junction quasi-reference electrode were used for voltammetric studies in dichloromethane, although the poten-

Table 1 Crystal and refinement data for complexes 11–14

	11	12	13	14
Formula	C ₂₃ H ₁₁ F ₁₀ O ₂ PPd	C ₄₆ H ₂₂ F ₂₀ O ₄ P ₂ Pd ₂	C ₄₁ H ₂₆ F ₁₀ O ₂ P ₂ Pd·0.48(C ₆ H ₆)·0.11(C ₆ H ₁₄)	C ₃₆ H ₂₂ Br ₂ F ₈ P ₂ Pd
fw	646.69	1293.38	955.57	934.69
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcn</i>
<i>a</i> (Å)	11.3594(9)	10.9599(16)	13.6907(10)	15.797(3)
<i>b</i> (Å)	14.5809(12)	18.571(3)	11.8192(9)	12.955(3)
<i>c</i> (Å)	14.5984(12)	22.210(3)	25.115(2)	16.382(3)
α (°)	75.895(2)			
β (°)	78.581(2)	90.025(3)	92.097(2)	
γ (°)	82.601(2)			
<i>V</i> (Å ³)	2290.4(3)	4520.4(12)	4061.3(5)	3352.8(11)
<i>Z</i>	4	4	4	4
<i>T</i> (K)	150(2)	150(2)	150(2)	200(2)
Colour, habit	Yellow, needle	Yellow, needle	Yellow, plate	Yellow, plate
Cryst dimens (mm ^{−3})	0.15 × 0.06 × 0.04	0.18 × 0.05 × 0.05	0.22 × 0.11 × 0.07	0.06 × 0.05 × 0.03
<i>D</i> _{calc} (g cm ^{−3})	1.875	1.900	1.563	1.852
μ (mm ^{−1})	0.982	0.995	0.620	3.104
No. indep. reflns (<i>R</i> _{int})	11 173 (0.044)	13 205 (0.081)	8374 (0.045)	3855 (0.047)
No. of obsd. reflns [<i>I</i> > 2 σ (<i>I</i>)]	8766	9322	6639	2719
No. params refined	667	688	605	222
<i>R</i> (<i>F</i> ²)	0.0309	0.0457	0.0348	0.0314
<i>R</i> _w (<i>F</i> ²)	0.0632	0.0755	0.0830	0.0683
$\rho_{\text{max}}/\rho_{\text{min}}$ (e Å ^{−3})	0.612/−0.551	0.746/−0.940	0.597/−0.427	0.642/−0.472

tials are quoted relative to the DmFc^{0/+} potential scale. The same reference electrode was used with the other techniques in dichloromethane, but a Ag/Ag⁺ (0.01 M AgNO₃, 0.1 M [*n*-Bu₄N][PF₆]) double junction quasi-reference electrode was used for studies in acetonitrile, with potentials again being calibrated to the DmFc^{0/+} scale. A glassy carbon (GC) working electrode with a diameter of 0.10 cm (area of 0.0072 cm²) or 0.30 cm (area of 0.071 cm²) was used for cyclic voltammetric experiments with scan rates of 50 to 1000 mV s^{−1}; the GC working electrode employed for rotating disc experiments and used with rotation rates of 500 to 3000 rpm had a diameter of 0.30 cm and an area of 0.071 cm², and was used in conjunction with a BAS RDE-2 accessory. A carbon fibre ultramicroelectrode (BAS, 5 micron radius or ALS, 25 micron radius) was used for steady state voltammetry. The areas or radii of the voltammetric working electrodes were determined from cyclic voltammograms using the peak current obtained from the oxidation of a 1.0 mM Fc solution (diffusion coefficient of 2.3 × 10^{−5} cm² s^{−1}) in CH₃CN (0.1 M [*n*-Bu₄N][PF₆]) or limiting current under steady state conditions and with the application of relevant equations, for instance, the Randles–Sevcik equation for transient voltammetry with macrodisk electrodes, and the Levich equation for rotating disk electrode (RDE) voltammetry.²⁵ Analysis of *n*-values for reduction processes from limiting current values at a microelectrode and RDE in acetonitrile were undertaken using a diffusion coefficient of 8.4 × 10^{−6} cm² s^{−1} which was the value derived from the reversible ferrocene process for 5. Spectroelectrochemical studies were undertaken with a Cary 5 UV-Visible-NIR spectrophotometer interfaced to a BAS model 100B electrochemistry system. UV-Visible spectra were obtained over the wavelength range of 200 to 800 nm and recorded continuously during the course of spectroelectrochemical experiments at a rate of 600 nm min^{−1}

until the electrolysis was completed. A Pt gauze working electrode and a Pt wire auxiliary electrode separated from the analyte solution by a fine porosity frit were located in an optically transparent quartz cell (1.0 mm optical path length). Bulk electrolyses were performed inside a nitrogen filled glove-box using a glassy carbon tube working electrode and a platinum gauze auxiliary electrode separated from the analyte solution by a fine porosity glass frit. Prior to each voltammetric experiment, the working electrode was polished with 0.3 μm alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler), rinsed with distilled water and dried with lint free tissue paper, and then rinsed with acetone and dried under nitrogen before being introduced into the glove-box. The solutions used under bench top conditions for voltammetric, spectroelectrochemical and bulk electrolysis measurements were purged with solvent-saturated nitrogen gas before each experiment and were blanketed with nitrogen gas during the experiment. All electrochemical experiments were carried out at ambient temperature (21 ± 1 °C).

Syntheses

[Pd(*O,O'*-hfacac)(κ²-2-C₆F₄PPh₂)] (11). To a solution of [Pd(*O,O'*-acac)(κ²-2-C₆F₄PPh₂)] (10) (250 mg, 0.46 mmol) in CH₂Cl₂ (5 mL) was added hexafluoroacetylacetone (10 drops). After stirring the mixture for 30 min, hexane (10 mL) was added and the solution was evaporated to dryness. The residue was dissolved in hexane (10 mL) containing hexafluoroacetylacetone (10 drops) and the extract was filtered through Celite. The filtrate was evaporated to dryness to give a pale yellow solid, which was dried *in vacuo* (284 mg, 95%). ¹H NMR: δ 6.14 (s, 1H, hfacac), 6.86–7.00 (m, 6H, aromatics), 7.57–7.68 (m, 4H, aromatics). ¹H NMR (CDCl₃): δ 6.21 (s, 1H, hfacac), 7.47–7.68 (m, 6H, aromatics), 7.77–7.90 (m, 4H, aromatics). ³¹P NMR:

δ -75.2 (m). ^{19}F NMR: δ -74.8 (s), -75.2 (s) (CF_3), -130.5 (m), -134.9 (m), -145.5 (m), -156.1 (m) ($\text{C}_6\text{F}_4\text{PPh}_2$). ESI-MS (m/z): 645.9 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{23}\text{H}_{11}\text{F}_{10}\text{O}_2\text{PPd}$: C 42.72, H 1.71, F 29.38. Found: C 42.79, H 1.81, F 29.15.

$[\text{Pd}_2(\text{O},\text{O}'\text{-hfacac})_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**12**). To a solution of $[\text{Pd}_2(\text{O},\text{O}'\text{-acac})_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**3**) (134 mg, 0.13 mmol) in CH_2Cl_2 (20 mL) was added hexafluoroacetylacetone (10 drops) and the mixture was stirred for 2 h. Hexane (5 mL) was added and the solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and hexane containing hexafluoroacetylacetone (10 drops) was added. On evaporation *in vacuo*, a bright yellow solid precipitated. This was filtered off, washed with hexane and dried (128 mg, 79%). ^1H NMR: δ 6.13 (s, 2H, hfacac), 6.75–7.41 (m, 16H, aromatics), 7.72–7.84 (m, 4H, aromatics). ^{31}P NMR: δ 25.8 (m). ^{19}F NMR: δ -74.3 (m), -75.2 (m) (CF_3), -109.2 (m), -118.6 (m), -145.1 (m), -156.7 (m) ($\text{C}_6\text{F}_4\text{PPh}_2$). ESI-MS (m/z): 1291.9 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{46}\text{H}_{22}\text{F}_{20}\text{O}_4\text{P}_2\text{Pd}_2$: C 42.72, H 1.71, F 29.38. Found: C 42.17, H 1.97, F 29.19.

$[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa\text{C-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\text{PPh}_3)]$ (**13**). To a solution of $[\text{Pd}(\text{O},\text{O}'\text{-hfacac})(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)]$ (**11**) (270 mg, 0.42 mmol) in CH_2Cl_2 (5 mL) was added solid PPh_3 (110 mg, 0.42 mmol), causing the solution to darken slightly. After 5 min, hexane was added. The yellow solid that precipitated on evaporation *in vacuo* was filtered off, washed with hexane and dried (370 mg, 97%). ^1H NMR: δ 5.88 (s, 1H, hfacac), 6.78–7.28 (m, 15H, aromatics), 7.45–7.82 (m, 10H, aromatics). ^{31}P NMR: δ -30.2 (br. m), 28.2 (br. m). ^{19}F NMR: δ -75.5 (br. s) (CF_3), -117.8 (m), -127.3 (m), -149.9 (m), -158.0 (m) ($\text{C}_6\text{F}_4\text{PPh}_2$). ESI-MS (m/z): 645.3 $[\text{M} - \text{PPh}_3]^+$. Anal. Calcd for $\text{C}_{41}\text{H}_{26}\text{F}_{10}\text{O}_2\text{P}_2\text{Pd}$: C 54.18, H 2.88, F 20.90. Found: C 54.62, H 3.12, F 21.00.

$[\text{PdBr}_2\{\text{PPh}_2(2\text{-C}_6\text{F}_4\text{H})_2\}]$ (**14**). (a) The solution obtained after bulk electrolysis of $[\text{Pd}_2(\mu\text{-Br})_2(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ was evaporated to dryness, the residue was dissolved in toluene and filtered through Celite to remove the supporting electrolyte. The filtrate was evaporated to dryness, dissolved in CH_2Cl_2 and treated with a solution of LiBr in MeOH . The solution was again evaporated to dryness and the residue dissolved in toluene. Filtration through Celite and evaporation of the filtrate gave a yellow/orange solid which was recrystallised from CH_2Cl_2 –hexane. ^1H NMR: δ 6.68–7.09 (m, 14H, aromatics), 7.56–7.96 (m, 8H, aromatics). ^{31}P NMR: δ 27.6 (m) (minor), 16.5 (m) (major). ^{19}F NMR: δ -118.8 (m), -136.1 (m), -146.9 (m), -152.2 (m) (minor), -119.7 (m), -137.7 (m), -149.8 (m), -153.6 (m) (major). HR TOF-MS (m/z): 854.9453 $[\text{M} - \text{Br}]^+$. Calcd for $\text{C}_{36}\text{H}_{22}\text{BrF}_8\text{P}_2\text{Pd}$: 854.9266.

(b) To a solution of *trans*- $[\text{Pd}(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]^4$ (90 mg, 0.12 mmol) in THF (5 mL) was added concentrated HBr (27 μL , ~ 0.25 mmol). The colourless solution immediately turned yellow then orange and after 5 min the solvent was removed *in vacuo*. The residue was recrystallised from CH_2Cl_2 –hexane to give a yellow/orange solid (84 mg, 77%). ^1H NMR: δ 0.89 (m, 0.6H, hexane), 1.23 (m, 0.8H, hexane), 6.60–7.10 (m, 14H, aromatics), 7.67–8.05 (m, 8H, aromatics). ^{31}P NMR: δ 16.5 (m). ^{19}F NMR: δ -119.7 (m), -137.7 (m), -149.7 (m),

-153.5 (m). HR TOF-MS (m/z): 854.9110 $[\text{M} - \text{Br}]^+$. Calcd for $\text{C}_{36}\text{H}_{22}\text{BrF}_8\text{P}_2\text{Pd}$: 854.9266.

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