ELSEVIER

Journal of Organometallic Chemistry 484 (1994) 113–118

Journal of Organometallic Chemistry

Pentafluorophenyl complexes of palladium and platinum containing chelating and bridging $Fe(C_5H_4PPh_2)_2$ or $Fe(C_5H_4SPh)_2$

Silverio Coco, Pablo Espinet *

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Received 14 March 1994

Abstract

Synthons of $M(C_6F_5)_2$ or $M(C_6F_5)X$ (M = Pd, X = Br; M = Pt, X = Cl) react with ferrocenyl compounds $Fe(C_5H_4PPh_2)_2$ (dppf) or $Fe(C_5H_4SPh)_2$ (dtpf) to give *cis*-$[M(C_6F_5)_2(L–L)]$ and *cis*-$[M(C_6F_5)X(L–L)]$ complexes of palladium and platinum. The *trans* geometry is obtained only when *trans*-$[Pd(C_6F_5)_2(tht)_2]$ reacts with dppf giving *trans*-$[\{Pd(C_6F_5)_2(dppf)\}_n]$. Removal of the halide from halopentafluorophenyl complexes with silver salts gives pentanuclear species $[(\mu\text{-dtpf})\{Pt(C_6F_5)(dtpf)\}_2][ClO_4]_2$ and $[(\mu\text{-dppf})\{Pd(Cl)(dppf)\}_2][ClO_4]_2$ when the reaction is carried out in the presence of dtpf and dppf, respectively. The use of selective ^{19}F homodecoupling allowed the determination of $^4J(^{31}P–^{19}F)$ for *cis*- and *trans*-$(C_6F_5)Pd$(phosphine) arrangements. Cyclic voltammetric studies on selected complexes usually show a reversible one-electron wave at about 1.0–1.2 V referred to ferrocene.

Keywords: Pentafluorophenyl; Palladium; Platinum; Electrochemistry; Ferrocene; NMR

1. Introduction

1,1'-Disubstituted ferrocene complexes $[Fe(C_5H_4E)_2]$, where E is a donor group such as PR_2 or SR (R = alkyl or aryl), have generated much interest as chelating [1] or *trans*-exobidentate ligands [2]. In particular, Ni, Pd and Rh complexes with $[Fe(C_5H_4PPh_2)_2]$ (dppf) exhibit high catalytic activity in olefin hydrogenation [3] and hydroformylation [4]. Moreover, some gold and platinum derivatives are possible antitumour agents [5]. Pd and Pt complexes with dppf and $[Fe(C_5H_4SPh)_2]$ (dtpf) are so far only of the type *cis*-$[Fe(C_5H_4L)_2MX_2]$ (X = halogen, L = PPh_2 or SPh) [1c,6,7] and derivatives obtained by substitution of the halogen [7–10].

In order to extend the chemistry of dppf and dtpf, we have analysed their *cis*- and *trans*-coordination toward pentafluorophenyl–palladium and –platinum complexes. These precursors were selected because they are easily available and, in the case of bis(pentafluorophenyl) derivatives, the geometry of the final complex is usually maintained after the reaction when two C_6F_5 groups are attached to the metal [11a]. In this paper, we report the synthesis, reactivity and electrochemistry of Pd and Pt complexes containing chelating and bridging dppf and dtpf and one or two C_6F_5 groups.

2. Results and discussion

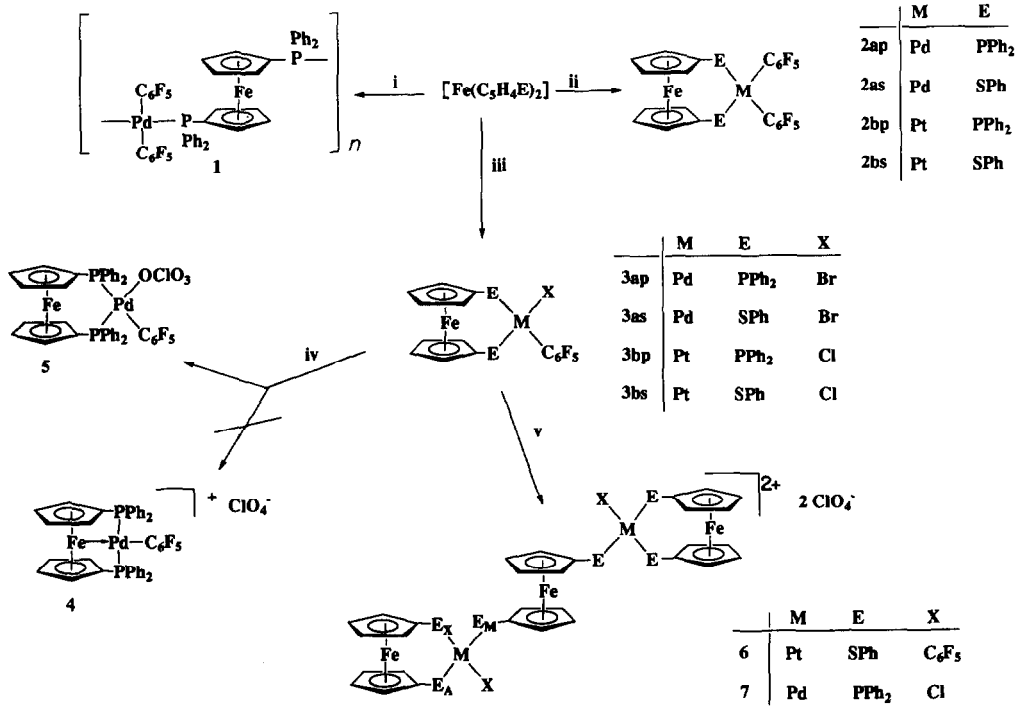
The reaction of *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (tht = tetrahydrothiophene) with dppf gives *trans*-$[Pd(C_6F_5)_2$-(dppf)] (**1**) (i, Scheme 1). Under the same conditions, no reaction is observed between *trans*-$[M(C_6F_5)_2(tht)_2]$ (M = Pd or Pt) and dtpf or between *trans*-$[Pt(C_6F_5)_2$-$(tht)_2]$ and dppf.

The IR spectrum of **1** (Table 1) indicates a *trans* arrangement of the C_6F_5 groups [11] and a polymeric structure is proposed, consistent with the insolubility of **1** in the usual solvents. This insolubility discouraged further pursuit of the synthesis of *trans* derivatives.

The reactions of dppf and dtpf with synthons of *cis*-$M(C_6F_5)_2$ and $M(C_6F_5)X$(M = Pd, X = Br; M = Pt, X = Cl) give the corresponding heterometallic complexes *cis*-$[M(C_6F_5)_2(dppf)]$ (M = Pd, **2ap**; M = Pt,

* Corresponding author.

SSDI 0022-328X(94)24725-X



Scheme 1. Reagents: (i) *trans*-$[Pd(C_6F_5)_2(tht)_2]$; (ii)$(NBu_4)_2[\{M(\mu\text{-}X)(C_6F_5)_2\}_2]$ + $2AgClO_4$ (M = Pd, X = Br; M = Pt, X = Cl); (iii) $[PdBr(C_6F_5)(CNCH_3)_2]$ or $[\{Pt(\mu\text{-}Cl)(C_6F_5)(tht)\}_2]$; (iv) $AgClO_4$; (v) $AgClO_4$ + $[Fe(C_5H_4E)_2]$ (E = PPh_2 or SPh); **7** is prepared similarly starting from $[PdCl_2(dppf)]$.

2bp); *cis*-$[M(C_6F_5)_2(dtpf)]$ (M = Pd, **2as**; M = Pt, **2bs**), *cis*-$[M(C_6F_5)X(dppf)]$ (M = Pd, X = Br, **3ap**; M = Pt, X = Cl, **3bp**) and *cis*-$[M(C_6F_5)X(dtpf)]$ (M = Pd, X = Br, **3as**; M = Pt, X = Cl, **3bs**) (ii, iii, Scheme 1), where the ferrocenyls are *cis*-chelating. Their IR spectra (Table 1) are consistent with the proposed geometry. There are two C_6F_5X-sensitive absorptions for complexes with two mutually *cis*-C_6F_5 groups, and only one for the rest of the complexes [11,12].

The ^{19}F NMR spectra (Table 2) of complexes **2** and **3** at room temperature show equivalence for the two F_{ortho} of the pentafluorophenyl groups. Even if the rotation of the C_6F_5 groups is restricted, [13], easy fluxional processes known to occur for the ferrocenes will cause the coordination plane to become a symmetry plane on the NMR time-scale. These fluxional processes are bridge reversal for dppf-derivatives [6], and also S-inversion for those with dtpf [14]. These dynamic processes can be frozen at low temperature. Fig. 1 illustrates the ^{19}F NMR spectra of **3bs** at different temperatures, revealing the inequivalence of the F_{ortho} at 260 K and their equivalence at 313 K.

Table 1
Yields, microanalytical data conductivities, molecular weights and selected IR spectral data

Complex	Formula	Yield (%)	Analysis [a]		M [a] or Λ_m [b]	IR (cm^{-1})	
			C(%)	H(%)		C_6F_5 [c]	Other bands
1	$[Pd(C_6F_5)_2(fdpp)]_n$	57	56.34(55.53)	2.67(2.81)	Insoluble	770	
2ap	$[Pd(C_6F_5)_2(fdpp)]$	66	55.77(55.53)	3.28(2.81)	925.2(994.0)	782, 771	
2bp	$[Pt(C_6F_5)_2(fdpp)]$	39	50.95(50.98)	2.50(2.77)	1015.7(1082.7)	779, 769	
2as	$[Pd(C_6F_5)_2(fdtp)]$	50	48.27(48.45)	1.96(2.37)	762.5(841.8)	789, 779	
2bs	$[Pt(C_6F_5)_2(fdtp)]$	75	43.94(43.83)	1.82(2.14)	956.6(930.8)	804, 794	
3ap	$[PdBr(C_6F_5)(fdpp)]$	44	53.20(52.92)	3.02(3.08)	917.4(907.0)	781	
3bp	$[PtCl(C_6F_5)(fdpp)]$	62	50.75(50.450	2.85(3.150)	1033.1(951.3)	793	300 [d]
3as	$[PdBr(C_6F_5)(fdtp)]$	73	45.01(44.50)	2.62(2.64)	730.1(755.2)	793	
3bs	$[PtCl(C_6F_5)(fdtp)]$	44	41.93(42.02)	2.12(2.50)	851.4(799.4)	806	332 [d]
5	$[Pd(C_6F_5)(OClO_3)(fdpp)]CHCl_3$	65	46.91(47.05)	2.70(2.77)		786	[e]
6	$[\{Pt(C_6F_5)(fdtp)\}_2(\mu\text{-}fdtp)][ClO_4]_2$	46	43.94(43.99)	2.69(2.53)	259 [b]	805	1099, 624 [f]
7	$[\{PdCl(fdpp)\}_2(\mu\text{-}fdpp)][ClO_4]_2$	42	57.51(57.10)	4.23(3.92)	263 [b]		1095, 624 [f]

[a] Calculated values in parentheses. [b] in acetone (5×10^{-4} mol cm^{-3}), values in S cm^2 mol^{-1}. [c] X-sensitive mode. [d] ν(Pt–Cl). [e] 1145, 1008, 635, 618 cm^{-1} ($OClO_3^-$). [f] ClO_4^-.

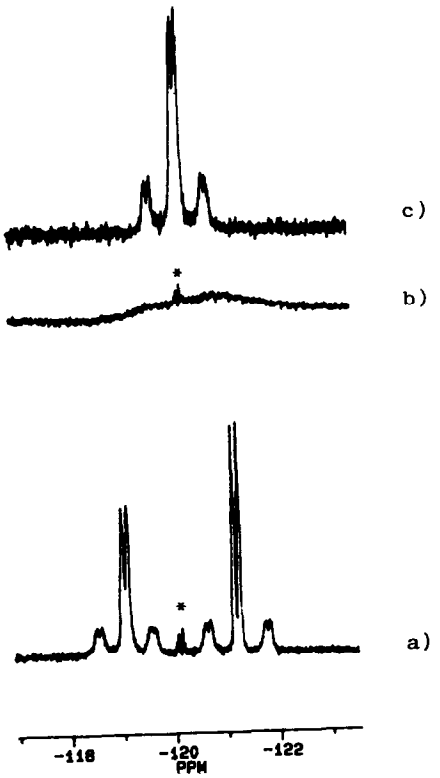


Fig. 1. ^{19}F NMR spectra (F_{ortho} region) of *cis*-[PtCl(C_6F_5)(dtpf)] (**3bs**) at different temperatures: (a) 260 K; (b) 293 K; (c) 313 K. The asterisks indicate an unidentified impurity.

Fig. 2. ^{19}F NMR spectra (F_{ortho} region) of *cis*-[PdBr(C_6F_5)(dppf)] (**3ap**): (a) coupled spectrum; (b) with selective decoupling of both the F_{meta} and the F_{para}.

In general the, F_{ortho} signals in the dppf derivatives are more complicated than in the dtpf complexes, owing to ^{19}F–^{31}P coupling. These coupling constants were measured for **3ap** by recording its ^{19}F NMR spectrum with selective decoupling of both the F_{meta} and the F_{para}. In this way the F_{ortho} signal, shown in Fig. 2(b), appears as a doublet of doublets with $J(F-P_{trans}) = 15.8$ Hz and $J(F-P_{cis}) = 8.0$ Hz.

Table 2
NMR data ($CDCl_3$) for the new compounds (shifts in ppm downfield relative to internal TMS (^1H) or external 85% H_3PO_4 in H_2O (^{31}P); coupling constants in Hz)

Complex	^1H NMR	^{19}F NMR
2ap	4.37 (m, 8H); 7.61–7.32 (m)	−116.25 (m, F_o); −162.32 (t, JF_p–F_m = 21, F_p); −163.40 (m, F_m)
2bp	4.35 (m, 4H); 4.42 (t, 4H; 7.66–7.33 (20H))	−118.36 (m, F_o; JPt–F = 300.2); −163.08 (t, JF–F_m = 21, F_p); −164.28(m, F_m)
2as	4.61 (t, 4H); 5.21 (t, 4H); 7.00 (10H)	−116.05 (m, F_o); −161.47 (t, JF_p–F_m = 21, F_p); −163.37 (m, F_m)
2bs	4.60 (t, 4H); 5.24 (t, 4H); 7.20 (s, 10H)	−118.59 (m, F_o; JPt–F = 424.8); −162.62 (t, JF_p–F_m = 21, F_p); −164.40 (m, F_m)
3ap	3.44 (m, 2H); 4.19 (m, 2H; 4.60 (m, 2H); 4.95 (m, 2H); 7.10–8.20 (20H)	−118.67 (m, F_o); −162.25 (t, JF_p–F_m = 21, F_p); −163.10 (m, F_m)
3bp	3.44 (m, 2H); 4.16 (m, 2H); 4.57 (m, 2H); 4.95 (m, 2H); 7.10–8.20 (20H)	−120.44 (m, F_o; JPt–F = 309.8); −163.13 (t, JF_p–F_m = 21, F_p); −164.08 (m, F_m)
3as	4.60 (m, 4H); 5.12 (m, 2H); 5.26 (m, 2H); 7.10–7.45 (10H)	−118.87 (m, F_o); −160.97 (t, JF_p–F_m = 20.3, F_p); −162.87 (m, F_m)
3bs	4.57 (m, 4H); 5.10 (m, 2H); 5.26 (m, 2H); 7.13–7.56 (10H) [a]	−120.19 (m, F_o; JPt–F = 311.35); −162.39 (t, JF_p–F_m = 21, F_p); −164.56 (m, F_m) [c]
5	3.39 (m, 2H); 4.18 (m, 2H); 4.58 (m, 2H); 4.92 (m, 2H); 7.04–7.79 (20H) [b]	−119.85 (m, F_o); −159.36 (t, JF_p–F_m = 21, F_p); −162.64 (m, F_m) [b]
6	3.65 (m, 8H); 4.74 (m, 4H); 5.21 (m, 4H); 7.09–7.40 (20H) [c]	−118.23 (m, F_o; JPt–F = 310.0); −159.46 (t, 21, F_p); −161.50 (m, F_m) [c]
7	3.41 (m, 8H); 3.99 (m, 4H); 4.26 (m, 4H); 4.77 (m, 4H); 4.89 (m, 4H); 6.90–7.90 (60H)	

[a] ^1H NMR (300 MHz); 4.57 (m, 2H); 4.60 (m, 2H); 5.10 (m, 2H); 5.26 (m, 2H); 7.13–7.56 (10H). [b] In CD_2Cl_2. [c] Spectra recorded at 313 K.

As a result of the $^{19}F-^{31}P$ coupling, the spin systems for the compounds are very complicated, and the $^{31}P\{^1H\}$ signals of **2** and **3** (Table 3) become one or two unresolved multiplets, respectively. For **3ap** the high-field signal is assigned to the phosphorus atom *trans* to the C_6F_5 group, because it is broader, as expected for stronger coupling to ^{19}F [11b]. For **3bp** the broader resonance, which is consequently assigned to the phosphorus atom *trans* to the C_6F_5 group, is the low-field signal. This assignment is confirmed by the smaller $^1J(Pt-P)$ observed for the low-field signal, as a consequence of the stronger *trans* influence of the C_6F_5 group compared to chlorine [15].

The ^1H NMR spectra (Table 2) of *cis*-[$M(C_6F_5)_2$(dtpf)] (M = Pd, **2as**; M = Pt, **2bs**) are typical of 1,1'-disubstituted ferrocene systems [1c,6,7]. Two slightly deshielded "triplets" are observed for the cyclopentadienyl ring protons. The low-field signal is assigned to the protons in the 2- and 5-positions of the ring, and the high field resonance to the protons in the 3- and 4-positions. These two signals overlap in the complexes *cis*-[$M(C_6F_5)_2$(dppf)] (M = Pd, **2ap**; M = Pt, **2bp**) and only a broad signal is detected [2c].

Similarly, the ^1H NMR spectra of complexes of type **3**, which have two inequivalent cyclopentadienyl rings, show four signals, or three when two of them overlap as in **3as** and **3bs**. This overlapping was resolved for **3bs** by recording the spectrum at 300 MHz. At this field, a COSY experiment (Fig. 3(a)) showed that the signals of each cyclopentadienyl ring alternate in chemical shift. For **3ap**, however, a COSY experiment (Fig. 3(b)) showed that the two high-field signals come from the same cyclopentadienyl ring, that *cis* to the C_6F_5 group, as proved by additional ^1H NMR experiments involving selective decoupling of each of the two different phosphorus atoms.

Attempts to extract the chlorine atom in complexes **3** with $AgClO_4$ were made, to induce the formation of a dative Fe → Pd bond as depicted in **4** (Scheme 1). The reactions led to complex mixtures which were not resolved. Only for **3ap** was the reaction clean, giving *cis*-[$Pd(OClO_3)(C_6F_5)$(dppf)] (**5**). The coordination of the perchlorate group is evident from its IR spectrum (Table 1) [16].

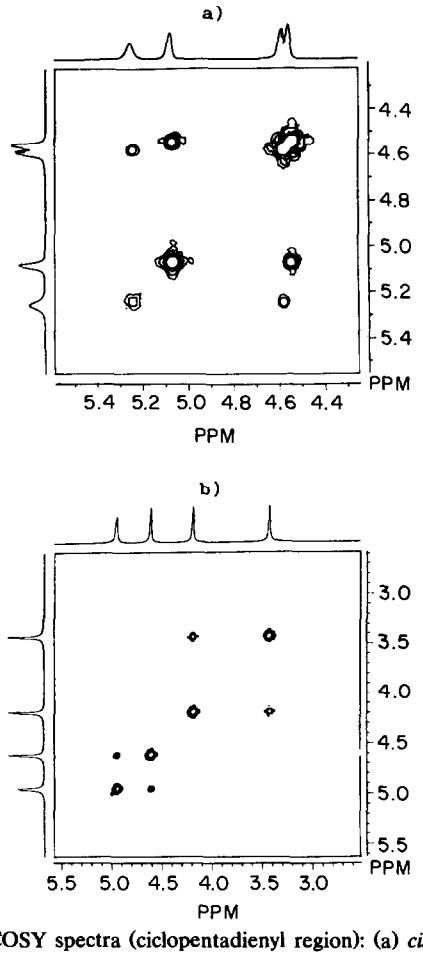


Fig. 3. COSY spectra (ciclopentadienyl region): (a) *cis*-[$PtCl(C_6F_5)$(dtpf)] (**3bs**); (b) *cis*-[$PdBr(C_6F_5)$(dppf)] (**3ap**).

As an example to check the use of these ferrocenes to produce complexes of higher nuclearity, we tested dtpf, which behaves as a ligand with less coordinating ability. The pentanuclear dicationic derivative [(μ-dtpf){$Pt(C_6F_5)$(dtpf)}$_2$][ClO_4]$_2$ (**6**) is isolated when chlorine extraction from **3bs** is carried out in the presence of dtpf (v, Scheme 1). The proposed geometry is supported by its molar conductivity, typical of a 1:2 electrolyte (Table 1) [17], and its IR spectrum which reveals ionic, non-coordinated ClO_4^-. The ^1H NMR spectrum of **6** is very temperature dependent, for the reasons discussed above. At 313 K it shows the same resonances as its precursor, and in addition another signal at greater field assigned to the bridging ferrocene ligand. Similarly, the reaction of $PdCl_2$(dppf) with one equivalent of $AgClO_4$ in the presence of dppf gives complex **7**.

The electrochemical behaviour of some of these complexes has been examined by cyclic voltammetry (Table 4). Complexes **2as**, **2bs**, **3ap** and **3bs** gave well defined one-electron reversible redox waves assigned

Table 3
$^{31}P\{^1H\}$ NMR data ($CDCl_3$) for the new compounds. (shifts in ppm downfield relative to external 85% H_3PO_4 in H_2O; coupling constants in Hz)

Complex	$^{31}P\{^1H\}$ NMR
2ap	15.60 (m)
2bp	8.47 (m, JPt–P = 1227.8)
3ap	20.40 (m); 37.40 (m)
3bp	16.11 (m, JPt–P = 2272.0); 13.29 (m, JPt–P = 3995.5)
5	18.23 (m); 39.7 (m) [a]
7	35.89 (dd, P_A); 26.75 (d, P_M, $J P_A-P_M$ = 15.3); 25.68 (d, P_X, $J P_A-P_X$ = 8.4)

[a] In CD_2Cl_2.

Table 4
Cyclic voltammetric data for the new compounds **2as**, **2bs**, **3ap**, **3as**, **3bs** and **6**

Complex	$E_{1/2}$ (V)
2as	1.07
2bs	1.12
3ap	1.00
3as	1.13 [a]
3bs	1.12
6	1.18

[a] Irreversible wave.

to the oxidation $Fe^{II} \rightarrow Fe^{III}$. A similar result was obtained for **6**, which showed a poorly resolved voltammogram due to the overlap of the waves of the two different ferrocenes. A one-electron irreversible wave was observed for **3as**. The $E_{1/2}$ values indicate that the complexes are oxidized at much higher anodic potential that the free ferrocenes, consistent with previous observations for related complexes [1c,7].

3. Experimental

3.1. General

Microanalyses (C, H, N) were carried out with a Perkin-Elmer 240B microanalyser. Molecular weights were determined with a Knauer apparatus in $CHCl_3$ and conductivities on a Crison 522 conductimeter. IR spectra were obtained on a Perkin-Elmer 883 instrument as mulls between polyethylene plates. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 80 and ^{19}F NMR spectra on a Bruker AC 300 instrument. Chemical shifts, in ppm, are positive downfield relative to internal TMS for ^1H, external H_3PO_4 for ^{31}P and $CFCl_3$ for ^{19}F. Cyclic voltammetric experiments were carried out using an AMEL 551 potentiostat–amperostat and a Tacussel GSTP signal generator in conjunction with a three-electrode cell, as described elsewhere [18]. Literature methods were used to prepare the starting materials *trans*-$[Pd(C_6F_5)_2(tht)_2]$ [12], $(NBu_4)_2[\{M(\mu\text{-}X)(C_6F_5)_2\}_2]$ (M = Pd, X = Br [12]; M = Pt, X = Cl [19]), $[PdBr(C_6F_5)(CNCH_3)_2]$ [11a], $[\{Pt(\mu\text{-}Cl)(C_6F_5)(tht)\}_2]$ [20], $[Fe(C_5H_4PPh_2)_2]$ [21], $[Fe(C_5H_4SPh)_2]$ [1c] and $[PdCl_2(dppf)]$ [7].

3.2. Preparation of trans-$[Pd(C_6F_5)_2(dppf)]$ (1)

To a solution of *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (0.038 g, 0.062 mmol) in $Et_2O/CHCl_3$ (5:1, 20 ml) was added dppf (0.038 g, 0.069 mmol) and the mixture was stirred for 2 h at room temperature. The resulting pale-orange precipitate of **1** was filtered off, washed with $CHCl_3$ (5 ml) and dried under vacuum.

3.3. Preparation of cis-$[Pd(C_6F_5)_2(dppf)]$ (2ap)

To a THF solution (20 ml) of $(NBu_4)_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ (0.070 g, 0.059 mmol) under dinitrogen was added $AgClO_4$ (0.025 g, 0.120 mmol). After stirring for 20 min, the suspension was evaporated to dryness and the residue was extracted with 50 ml of diethyl ether. The resulting solution was concentrated under vacuum to ca. 2 ml, then THF (20 ml) and dppf (0.040 g, 0.072 mmol) were added. The solution was stirred for 2 h at room temperature. The solvent was removed and the residue was dissolved in a minimum amount of CH_2Cl_2, then hexane was added and **2ap** precipitated as a yellow powder, which was recrystallized from Et_2O.

Compounds **2bp**, **2as** and **2bs** were obtained similarly as yellow microcrystals.

3.4. Preparation of cis-$[PdBr(C_6F_5)(dppf)]$ (3ap)

To a solution of $[PdBr(C_6F_5)(CH_3CN)_2]$ (0.047 g, 0.108 mmol) in THF (20 ml) was added dppf (0.060 g, 0.108 mmol) and the solution was stirred for 1 h at room temperature. The solvent was removed and the residue was dissolved in a minimum amount of CH_2Cl_2, then hexane was added and **3ap** precipitated as a yellow powder, which was recrystallized from CH_2Cl_2/hexane.

Compound **3as** was obtained similarly. Compounds **3bp** and **3bs** were prepared from $[\{Pt(\mu\text{-}Cl)(C_6F_5)(tht)\}_2]$ and the corresponding ferrocene as described for **3ap**.

3.5. Preparation of cis-$[Pd(C_6F_5)(OClO_3)(dppf)]$ (5)

To a solution of **3ap** (0.200 g, 0.220 mmol) in toluene (30 ml) was added a solution of $AgClO_4$ (0.049 g, 0.236 mmol) in 10 ml of toluene. The mixture was stirred for 1 h in the dark. The solvent was removed, the residue was extracted with $CHCl_3$ (20 ml) and the insoluble AgBr was filtered off. Concentration of the solution to a few ml afforded **5** as orange crystals.

3.6. Preparation of $[(\mu\text{-dtpf})\{Pt(C_6F_5)(dtpf)\}_2][ClO_4]_2$ (6)

To a solution of **3bs** (0.060 g, 0.086 mmol) in CH_2Cl_2 (20 ml) was added $AgClO_4$ (0.018 g, 0.087 mmol) in 10 ml of CH_2Cl_2. After stirring for 45 min in the dark, the precipitate of AgCl was filtered off and dtpf (0.024 g, 0.044 mmol in 10 ml of CH_2Cl_2) was added to the filtrate. Stirring for 2 h, concentration to small volume and addition of diethyl ether afforded **6** as an orange solid.

3.7. Preparation of $[(\mu\text{-dppf})\{PdCl(dppf)\}_2][ClO_4]_2$ (7)

This compound was obtained from $PdCl_2$(dppf) (0.120 g, 0.164 mmol), $AgClO_4$ (0.034 g, 0.164 mmol) and dppf (0.045 g, 0.081 mmol) as a violet solid as described for **6**.

Acknowledgements

We thank the Spanish Dirección General de Investigación Científica y Técnica for financial support (PB89-0360) and Dr. G. García-Herbosa for the cyclic voltammetric measurements.

References

[1] (a) See, for example: (a) W.R. Cullen and J.D. Woollins, *Coord. Chem. Rev., 39* (1981) 1; (b) W.H. Watson, A. Nagl, S. Hwang and M.G. Richmond, *J. Organomet. Chem., 445* (1993) 163; (c) B. McCulloch, D.L. Ward, J.D. Woolins and C.H. Brubaker, Jr., *Organometallics, 4* (1985) 1425; (d) G. Bandoli, G. Trovó, A. Dolmella and B. Longato, *Inorg. Chem., 31* (1992) 45; (e) B.S. Haggerty, C.E. Housecroft, A.L. Rheingold and B.A.M. Shaykh, *J. Chem. Soc., Dalton Trans.*, (1991) 2175; (f) M. Sato, H. Shigeta, M. Sekino and S. Akabori, *J. Organomet. Chem., 458* (1993) 199; (g) M. Sato and M. Sekino, *J. Organomet. Chem., 444* (1993) 185; (h) S. Onaka, H. Furuta and S. Takagi, *Angew. Chem., Int. Ed. Engl., 32* (1993) 87; (i) M. Sato and M. Sekino, *J. Organomet. Chem., 444* (1993) 185.

[2] (a) H.S.O. Chan, T.S.A. Hor, L.-T. Phang and K.L. Tan *J. Organomet. Chem., 407* (1991) 353; (b) P.M.N. Low, Y.K. Yan, H.S.O. Chan and T.S.A. Hor, *J. Organomet. Chem., 454* (1993) 205; (c) L.-T. Phang, S.C.F. Au-Yeung, T.S.A. Hor, S.B. Khoo, Z.-Y. Zhou and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1993) 165; (d) L.-T. Phang, K.-S. Gan, H.K. Lee and T.S.A. Hor, *J. Chem. Soc., Dalton Trans.*, (1993) 2697; (e) M.C. Gimeno, A. Laguna, C. Sarrosa and P.G. Jones, *Inorg. Chem.*, (1993) 5926.

[3] T. Hayashi and M. Kumada, *Acc. Chem. Res., 15* (1982) 395.

[4] (a) O.H. Hughes and J.D. Unruh, *J. Mol. Catal., 12* (1981) 71; (b) J.D. Unruh and J.R. Chistenson, *J. Mol. Catal., 14* (1982) 19.

[5] (a) D.T. Hill, G.R. Girard, F.L. McGabe, R.K. Johnson, R.D. Slupik, J.H. Zhang, W.M. Reiff and D.S. Eggleston, *Inorg. Chem., 28* (1989) 352; (b) C.K. Mirabelli, D.T. Hill, L.F. Fancette, F.L. McCabe, G.R. Girard, D.B. Bryan, B.M. Sutton, J.O. Bartus, S.T. Crooke and R.K. Johnson, *J. Med. Chem., 30* (1987) 2181.

[6] I.R. Batter, W.R. Cullen, T.J. Kim, J.R. Steven and *J. Trotter, Organometallics, 4* (1985) 972.

[7] D.A. Clemente, G. Pilloni, B. Corain, B. Longato and C. Tiripicchio, *Inorg. Chim. Acta, 115* (1986) L9.

[8] B. Longato, G. Pilloni, G. Valle and B. Corain, *Inorg. Chem., 27* (1988) 956.

[9] G.M. Whitesides, J.G. Gaash and E.R. Stedrousky, *J. Am. Chem. Soc., 94* (1972) 5258.

[10] M. Sato, M. Sekino and S. Akabori, *J. Organomet. Chem., 344* (1988) C31.

[11] (a) R. Usón, J. Forniés, J.A. Nalda, M.J. Lozano, P. Espinet and A.C. Albeniz, *Inorg. Chim. Acta, 156* (1989) 251; (b) R. Usón, J. Forniés, P. Espinet, R. Navarro and C. Fortuño, *J. Chem. Soc., Dalton Trans.*, (1987) 2077; (c) R. Usón and J. Forniés, *Adv. Organomet. Chem., 28* (1988) 219.

[12] R. Usón, J. Forniés, F. Martinez and M. Tomas, *J. Chem. Soc., Dalton Trans.*, (1980) 888.

[13] A.C. Albéniz, J.C. Cuevas, P. Espinet, J. de Mendoza and P. Prados, *J. Organomet. Chem., 410* (1991) 257.

[14] K.G. Orrell, V. Sik, C.H. Brubaker, Jr. and B. McCulloch, *J. Organomet. Chem., 276* (1984) 267.

[15] F.S.M. Hassan, D.M. McEwan, P.G. Pringle and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1985) 1501.

[16] J. Peone, Jr., and L. Vaska, *Angew. Chem., Int. Ed. Engl., 10* (1971) 511.

[17] W.J. Geary, *Coord. Chem. Rev., 7* (1971) 81.

[18] P. Espinet, G. García-Herbosa and J.M. Ramos, *J. Chem. Soc., Dalton Trans.*, (1990) 2931.

[19] R. Usón, J. Forniés, M. Tomas and B. Menjón, *Organometallics, 5* (1986) 1581.

[20] R. Usón, J. Forniés, P. Espinet and G. Alfranca, *Synth. React. Inorg. Met. Org. Chem., 10* (1980) 579.

[21] J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenberg, R.E. Merrill and J.C. Smart, *J. Organomet. Chem., 27* (1971) 241.