Synthesis of palladium cyclopentadienyl complexes. Decamethylpalladocene dication [Pd(η^5-C$_5$Me$_5$)]$^{2+}$

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Abstract

The palladium pentamethylcyclopentadiene complex [Pd(η^4-C$_5$Me$_5$H)Cl$_2$] (1) reacted with AgBF$_4$, in the presence of 1,5-cyclooctadiene or pentamethylcyclopentadiene, to give the cationic compounds [Pd(η^4-diene)(C$_5$Me$_5$)]$^+$BF$_4^-$ (diene = C$_8$H$_{12}$ (2) or C$_5$Me$_5$H(3)). The cyclopentadienyl complex [Pd(η^4-C$_5$Me$_5$H)(η^5-C$_5$H$_5$)]$^+$BF$_4^-$ (4) was prepared by the action of a mixture of CpTl and TlBF$_4$ on 1 in acetone solution. Cyclic voltammetry showed that all three complexes 2–4 can be oxidized and reduced. The oxidation of 3 with (NH$_4$)$_2$[Ce(NO$_3$)$_6$] leads to the first palladocene; the decamethylpalladocene dication [Pd(η^5-C$_5$Me$_5$)$_2$]$^{2+}$(BF$_4^-$)$_2$ (5).

1. Introduction

Biscyclopentadienyl complexes (metallocenes) are known for most transition metals, but attempts to prepare palladocenes and platinocenes were unsuccessful. Recently, however, the first platinocenes, the pentamethyl- and decamethyl-platinocene dications [Pt(η^5-C$_5$Me$_5$)(η^5-C$_5$R$_5$)]$^{2+}$ (R = H or Me) were prepared by both chemical [1] and electrochemical [2] methods. The reduction of [Pt(η^5-C$_5$Me$_5$)$_2$]$^{2+}$ to the 19-electron cation radical is followed by a fast chemical reaction which results in the formation of [Pt(η^4-C$_5$Me$_5$H)(η^5-C$_5$Me$_5$)]$^+$ [2]. The high reactivity of the 19-and 20-electron palladocenes and platinocenes by comparison with the nickel analogues is probably the reason why these metallocenes were not isolated from reactions of Pd(II) and Pt(II) salts with sodium cyclopentadienide [3]. However, as for platinum, the methylated palladocene dications should be more stable and it should therefore be possible to synthesize them. We have now succeeded in this and here report the synthesis of η^4-cyclopentadiene-η^5-cyclopentadienylpalladium complexes and of the decamethylpalladocene dication.

2. Results and discussion

Complexes of Pd(IV) analogous to [Pt$_2$(η^5-C$_5$Me$_5$)$_2$(μ-Br)$_3$]$^{3+}$ [1,4], which would be suitable for the preparation of palladocene dications, are not known; thus an alternative synthetic strategy, recently adopted for the platinum complexes [2], the oxidation of η^4-pentamethylcyclopentadiene complexes [Pd(η^4-C$_5$Me$_5$H)(η^5-C$_5$R$_5$)]$^+$, was used instead. The complex [Pd(η^4-C$_5$Me$_5$H)Cl$_2$] (1), prepared as described earlier [5], was used as starting material for the synthesis of diene(cyclopentadienyl)palladium complexes.

Freshly prepared 1 is a mixture of *endo*-H and *exo*-H isomers, like the analogous platinum compound [6,7] (Scheme 1). In the ^{1}H NMR spectrum of 1 two sets of resonances were observed (δ): δ 1.10 (d, 3H, Me, J = 6.6 Hz), 1.70 (s, 6H, 2Me); 2.27 (s, 6H, 2Me); 3.74 (q, 1H, J = 6.6 Hz) (*endo*-H isomer); 1.65 (s, 6H, 2Me); 1.88 (d, 3H, Me, J = 7.3 Hz); 2.38 (s, 6H, 2Me); 3.31(q, 1H, J = 7.3 Hz) (*exo*-H isomer) ppm. It may be noted that the *exo*-hydrogen of 1 resonates at higher field relative to the *endo*-hydrogen, as was observed for [Pt(η^4-C$_5$Me$_5$H)Cl$_2$] [7]. This is rather unusual for cyclopentadiene complexes of second- and third-row transition metals, where the chemical shifts of the *exo*-H atoms are normally at lower field than the *endo*-H

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Scheme 1.

2. diene = C_8H_{12}
3. diene = C_5Me_5H

Scheme 2.

Scheme 3.
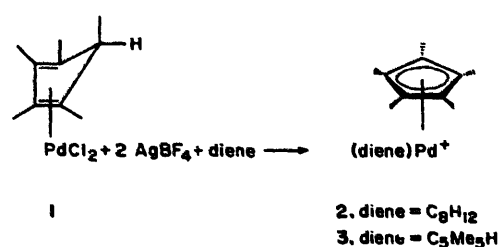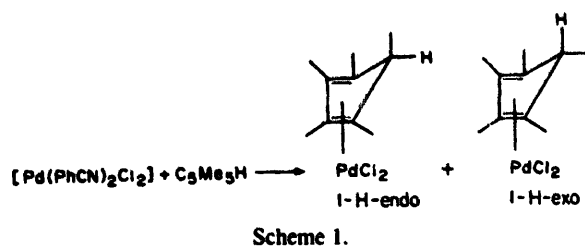
atoms [7]. The *exo*-H isomer **1** is less stable than the analogous *endo*-H isomer or *exo*-H isomer of the platinum complex $[Pt(\eta^4-C_5Me_5H)Cl_2]$; it decomposed readily and could not be purified or transformed into a stable derivative.

2.1. Synthesis of palladium diene monocations

The formation of a solvate dicationic complex $[Pd(\eta^4-C_5Me_5H)(acetone)_x]^{2+}(BF_4)_2$ was not detected in the reaction of **1** with $AgBF_4$ in acetone owing to its lower stability by comparison with the platinum analogue [6,8]. Nevertheless the same reaction carried out in the presence of either cycloocta-1,5-diene or pentamethylcyclopentadiene gave the cationic complexes **2** or **3** with a 40-50% yield (Scheme 2).

Compounds **2** and **3** were characterized by microanalysis and spectroscopically. The complex **2** showed a sharp singlet in the ^1H NMR spectrum at $\delta = 1.98$ ppm owing to the cyclopentadienyl ring protons and multiplets at $\delta = 2.65$ and 5.15 ppm owing to the cyclooctadiene methylene and olefinic protons. In the NMR spectra of **3** the signals of C_5Me_5 were observed at $\delta = 1.85$ (^1H), and 9.22, 111.7 (^{13}C) ppm respectively, while those of the CHMe group of η^4-pentamethylcyclopentadiene were observed at $\delta = 0.79$ (d, CH_3), 3.40 (q, H) and 25.1 (CH*Me*), 58.7 (CHMe) ppm, whereas the η^4-C_4Me_4 moiety was found at $\delta = 1.75$ (2Me), 2.28 (2Me) (^1H), and 10.6 (C*Me*), 11.8 (C*Me*), 105.9 (C*Me*), and 111.7 (C*Me*) (^{13}C) ppm.

The complex $[Pd(\eta^4-C_5Me_5H)(\eta^5-C_5H_5)]^+BF_4^-$ (**4**) was formed when cyclopentadiene rather than pentamethylcyclopentadiene was used in this reaction. However, in this case, one other cationic complex of unknown structure was also formed. In the ^1H NMR spectrum of the mixture, there are four multiplets of equal intensity in the region $\delta = 4.9$–6.6 ppm (which
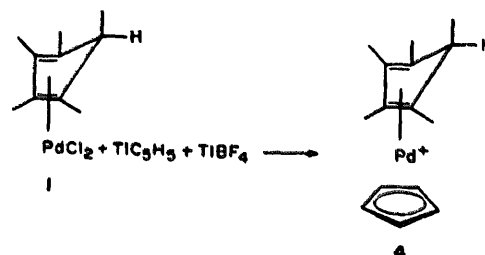
are characteristic of substituted cyclopentadienes) as well as the resonances of **4**. As it was impossible to separate the mixture of these two cationic complexes another method of synthesis of **4** was used; this consisted of reacting **1** with thallium cyclopentadenide in the presence of $TlBF_4$ (Scheme 3).

Complex **4** was prepared in this way with 40% yield and was characterized by NMR spectra. The chemical shifts of the methyl protons of the η^4-pentamethylcyclopentadiene CH*Me* at $\delta = 0.82$ (^1H) and 25.8 (^{13}C) ppm as well as C*H*Me at 3.81 ppm suggest that complex **4** is the *endo*-H isomer.

2.2. Cyclic voltammetry study of cationic complexes 2–4: oxidation of $[Pd(\eta^4-C_5Me_5H)(\eta^5-C_5Me_5)]^+$

Cyclic voltammetry (CV) studies (Table 1) of **2–4** were carried out in tetrahydrofuran (THF) solutions on carbon glass electrodes using Bu_4NPF_6 as supporting electrolyte. The data show that **2–4** are capable of both oxidation and reduction, and that the reductions of all three complexes are irreversible one-electron processes. The values of the reduction peak potentials depend on the number of methyl substitutents on the cyclopentadienyl ring; thus $[Pd(\eta^4-C_5Me_5H)(\eta^5-C_5H_5)]^+BF_4^-$ (**4**) is

Table 1

CV data for $[M(\eta^4\text{-diene})(\eta^5\text{-}C_5R_5)]^+ BF_4^+$ (M = Pd or Pt) ($c = 2 \times 10^{-3}$ M l^{-1}; THF, 0.1 M Bu_4NBF_4; v = 200 mV s^{-1}; reference electrode SCE)

	E_{pa} (V)		E_{pc} (V)	
	Pd	Pt [2]	Pd	Pt [2]
$[M(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}C_5Me_5)]^+$	+0.93, +1.42	+1.63, +1.93	−1.03	−1.51
$[M(\eta^4\text{-}C_5MeH)(\eta^5\text{-}C_5Me_5)]^+$	+1.23	+1.34	−1.02	−1.44
$[M(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+$	+1.65	+1.76	−0.70	−1.24
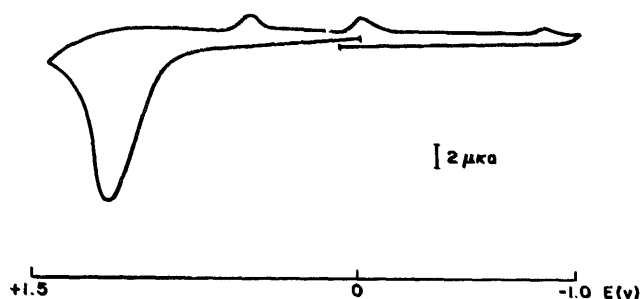
Fig. 1. Cyclic voltammogram of [Pd(η⁴-C₅Me₅H)(η⁵-C₅Me₅)]⁺ BF₄⁻ (3) in THF (ν = 200 mV s⁻¹).
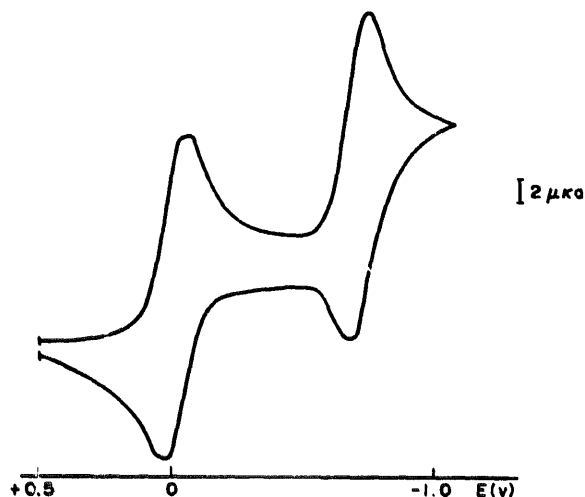
Fig. 2. Cyclic voltammogram of [Pd(η⁵-C₅Me₅)₂]⁺ BF₄⁻ (3) in acetone (ν = 200 mV s⁻¹).

Scheme 4.

reduced more easily than 2 and 3. The reduction potentials of the palladium complexes are less negative by 0.4–0.7 V by comparison with the platinum analogues [2].

Two oxidation peaks were observed for the cyclooctadiene complex 2. The first irreversible peak was at +0.93 V and is less positive than the peak potentials of 3 (ΔE_{pa} = 0.3 V) and [Pt(η⁴-C₈H₁₂)(η⁵-C₅-Me₅)]⁺(ΔE_{pa} = 0.8 V) [2]. One additional irreversible peak, observed for 2 at +1.42 V, is probably due to products of decomposition of the dication radical [Pd(η⁴-C₈H₁₂)(η⁵-C₅Me₅)].

Both 3 and 4 oxidize by irreversible one-electron processes, which proceed slightly more easily (by 0.1–0.2 V), compared with the analogous platinum complexes. The 17-electron dication radicals first formed by
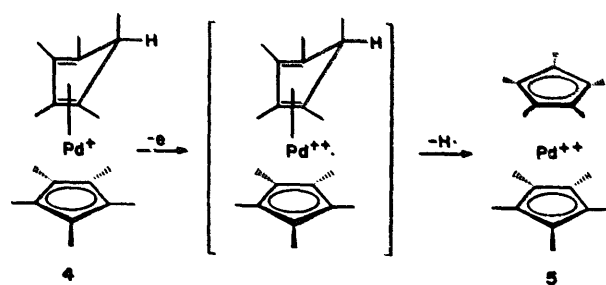
oxidation of 3 and 4 are unstable on the CV time scale, as shown by the irreversibility of the peaks. They are unstable chemically because of the appearance of new reduction peaks, at −0.14 and +0.30 V respectively, after preliminary anodic polarization (Fig. 1); if the initial complexes are not oxidized first, those peaks are not observed. By analogy with the oxidation of [Pt(η⁴-C₅Me₅H)(η⁵-C₅Me₅)]⁺ [2], it can be proposed that the dication radical formed on oxidation of 3 undergoes homolytic C–H bond scission at the sp³-hybridized carbon atom of the η⁴-C₅Me₅H ligand to give the decamethylpalladocene dication.

We find that bulk electrolysis of 3 at +1.5 V (carbon glass electrode, acetone, 0.1 M NaBF₄ or 0.1 M Bu₄NPF₆) actually leads to formation of [Pd(η⁵-C₅Me₅)₂]²⁺ (5), but the yields are very low (3–5%) (Scheme 4). Chemical oxidation of 3 with cerium(IV) ammonium nitrate in acetone is a better way to make the dication 5, which can be obtained with a 38% yield. Neither chemical nor electrochemical oxidation of 4 gave any stable products.

The decamethylpalladocene dication 5 was characterized by microanalysis, fast atom bombardment (FAB) mass spectroscopy (MS), ¹H and ¹³C NMR spectroscopy. A singlet at δ = 2.32 ppm was observed in the ¹H NMR spectrum and at δ = 9.3 and 123.5 ppm in ¹³C NMR spectrum. CV of 5 showed two reversible one-electron peaks at −0.08 and −0.78 V (Fig. 2). The CV data suggest that both the 19-electron cation radical [Pd(η⁵-C₅Me₅)₂]⁺ and the 20-electron neutral [Pd(η⁵-C₅Me₅)₂] decamethylpalladocene are stable on the time scale of the CV method (scan rate, 200 mV s⁻¹; T = 20°C). Notwithstanding that, all attempts to carry out bulk electrolysis of 5 at the first plateau and the second plateau were unsuccessful, and no formation of stable organometallic species was observed. The direct interac-

Table 2
Reduction potentials for the 18-electron-to-19-electron transition in the Group VIII metallocenes [M(η⁵-C₅R₅)₂]ⁿ⁺

Metallocene	E^{red} (V)	Metallocene	E^{red} (V)	Metallocene	E^{red} (V)
Cp₂Fe [9]	−3.01	Cp₂*Co⁺ [11]	−1.47	Cp₂*Ni²⁺ [11]	+0.31
Cp₂Ru [10]	−3.48	Cp₂*Rh⁺ [12]	−1.82	Cp₂*Pd²⁺	−0.08
Cp₂Os [10]	−3.44	Cp₂*Ir⁺ [13]	−2.27	Cp₂*Pt²⁺ [1,2]	−0.60

tion of either PdCl$_2$ or Pd(acac)$_2$ with two equivalents of Me$_5$C$_5$MgCl x-THF did not give any identifiable products either.

Since the decamethylpalladocene dication 5, which is the last unknown metallocene of group VIII, is now available, a comparison of the properties of all nine metallocenes can be made. Reduction potentials for the 18-electron-to-19-electron transition are collected in Table 2 for [M(η^5-C$_5$H$_5$)$_2$]–[M(η^5-C$_5$H$_5$)$_2$]$^-$ (M = Fe [9], M = Ru [10] or Os [10]). [M(η^5-C$_5$Me$_5$)$_2$]$^+$–[M(η^5-C$_5$Me$_5$)$_2$] (M = Co [11], M = Rh [12] or Ir [13]) and [M(η^5-C$_5$Me$_5$)$_2$]$^{2+}$–[M(η^5-C$_5$Me$_5$)$_2$]$^+$ (M = Ni [11]; M = Pd or Pt [4]). While the comparison of these reduction potentials is not rigorous (since the potentials compared relate to both reversible and irreversible processes as well as to different solvents and temperatures), we believe that the regularities observed are valid and can be summarized as follows.

The difference between the reduction potentials of neighbouring metallocenes within each of transition metals in a row is approximately 1.7 V and is independent of charge; the only exception is osmocene. The difference between the reduction potentials of neighbouring complexes in each column is approximately 0.4 V, only osmocene again being an exception.

From the electrochemical data, one can derive two generalizations.

(a) The stability of 19-electron metallocenes is related to the reduction potentials of the 18-electron precursors; the more positive the latter, the more stable are the 19-electron compounds formed,

(b) The stability is reduced on moving both from left to right in each row and from top to bottom in each column (Table 2).

The following examples illustrate these generalizations.

In the Ru, Rh, Pd row, (i) ruthenocene reduces irreversibly at room temperature, the process becoming reversible at −60°C [10], (ii) the reduction peak of [Rh(η^5-C$_5$Me$_5$)$_2$]$^+$, quasi-reversible at room temperature, becomes reversible at −30°C [12], and (iii) the reduction of [Pd(η^5-C$_5$Me$_5$)$_2$]$^{2+}$ is reversible even at room temperature.

In the Ni, Pd, Pt triad, the 19-electron nickelocene monocation is stable on both the preparative and the CV time scales, while the palladium analogue [Pd(η^5-C$_5$Me$_5$)$_2$]$^+$ is stable on the CV time scale but could not be isolated (as noted above) and the 19-electron [Pt(η^5-C$_5$Me$_5$)$_2$]$^+$ is not stable on either the preparative or the CV time scales.

3. Experimental details

All experiments were performed under argon in solvents purified by standard methods. Cyclic voltammetry

measurements were made with potentiostat Pl-50-i on a carbon glass electrode in solutions using 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte, scan rate 200 mV s^{-1} and peak potentials were recorded with reference to a saturated calomel electrode (SCE). ^{1}H and ^{13}C NMR spectra were obtained with a Bruker-WP-200-SY and Bruker-AMX-400 spectrometers. All chemical shifts are reported with reference to tetramethylsilane.

3.1. Synthesis of [Pd(η^4-C$_5$Me$_5$H)Cl$_2$] (1) [5]

1,2,3,4,5-Pentamethylcyclopentadiene (1.06 g, 7.79 mmol) was added to a solution of [Pd(NCPh)$_2$Cl$_2$] (2.00 g, 5.21 mmol) in benzene (240 cm^3). The resultant precipitate was filtered off, washed with pentane (3 × 20 cm^3) and dried in vacuo, to give 1 (yield, 1.10 g (67%)). ^{1}H NMR (acetone-d_6): δ 1.10 (d, 3H, CH$_3$, J = 6.6 Hz); 1.70 (s, 6H, 2 CH$_3$); 2.27 (s, 6H, 2 CH$_3$); 3.74 (q, 1H, J = 6.6 Hz) (endo-H isomer); 1.65 (s, 6H, 2 CH$_3$): 1.88 (d, 3H, CH$_3$, J = 7.3 Hz); 2.38 (s, 6H, 2 CH$_3$); 3.31 (q, 1H, J = 7.3 Hz) (exo-H isomer) ppm.

3.2. Reaction of 1 with dienes to give 2–4 (general procedure)

Silver tetrafluoroborate (0.12 g, 0.60 mmol) was added to a solution of 1 (0.09 g, 0.30 mmol) and diene (1.20 mmol) in acetone (10 cm^3) at −78°C. The mixture was stirred 10 min., allowed to warm to room temperature, stirred 0.5 h and then filtered. The filtrate was concentrated, and diethyl ether (30 cm^3) was added, to give a precipitate that was filtered off, washed with ether, crystallized from CH$_2$Cl$_2$–EtO and dried in vacuo.

3.2.1. [Pd(η^4-C$_8$H$_{12}$)(η^5-C$_5$Me$_5$)]$^+$BF$_4^-$ (2).

Yield, 0.06 g (46%) 2. Anal. Found: C, 48.2; H, 6.2; F, 17.3. C$_{18}$H$_{27}$BF$_4$Pd Calc.: C, 49.5; H, 6.2; F, 17.4%. ^{1}H NMR (acetone-d_6): δ 1.98 (s, 15H, C$_5$Me$_5$); 2.65 (m, 8H, 4CH$_2$); 5.15 (m, 4H, 4CH) ppm.

3.2.2. [Pd(η^4-C$_5$Me$_5$H)(η^5-C$_5$Me$_5$)]$^+$BF$_4^-$ (3).

Yield 0.06 g (46%) 3. Anal. Found: C, 51.4; H, 6.7. C$_{20}$H$_{31}$BF$_4$Pd Calc.: C, 51.7; H, 6.7%. ^{1}H NMR (acetone-d_6): δ 0.79 (d, 3H, CH$_3$, J = 6.5 Hz); 1.75 (s, 6H, 2CH$_3$); 1.85 (s, 15H, C$_5$Me$_5$); 2.28 (s, 6H, 2CH$_3$); 3.40 (q, 1H, J = 6.5 Hz) ppm. ^{13}C NMR (acetone-d_6): δ 9.2 (C$_5$Me$_5$); 10.6 (2Me); 11.8 (2Me); 25.1 (CH Me); 58.7 (CHMe); 105.9 (CMe); 111.7 (CMe); 111.8 (C$_5$Me$_5$) ppm.

3.3. Preparation of [Pd(η^4-C$_5$Me$_5$H)(η^5-C$_5$H$_5$)]$^+$BF$_4^-$ (4)

Thallium cyclopentadienide (0.25 g, 0.86 mmol) and thallium tetrafluoroborate (0.23 g, 0.86 mmol) were

added to a solution of 1 (0.27 g, 0.86 mmol) in acetone (30 cm^3). The mixture was stirred for 30 min at room temperature and then filtered. The filtrate was concentrated, and diethyl ether (20 cm^3) was added. The precipitate was filtered off, washed with ether and dried in vacuo. The product was dissolved in water (15 cm^3) and NH$_4$PF$_6$ added: crystallization of the precipitate from CH$_2$Cl$_2$–Et$_2$O gave 4 (yield, 0.17 g (44%)). Anal. Found: C, 39.7; H, 4.7. C$_{15}$H$_{21}$F$_6$PPd Calc.: C, 39.8; H, 4.7%. ^{1}H NMR (acetone-d_6): δ 0.82 (d, 3H, CH$_3$, J = 6.6 Hz); 2.11 (s, 6H, 2CH$_3$); 2.53 (s, 6H, 2CH$_3$); 3.81 (q, 1H, J = 6.6 Hz); 6.05 (s, 5H, C$_5$H$_5$) ppm. ^{13}C NMR (acetone-d_6): δ 12.3 (2Me); 15.8 (2Me); 25.8 (CHMe); 60.6 (CHMe); 101.3 (C$_5$H$_5$); 110.3 (CMe); 119.7 (CMe) ppm.

3.4. Oxidation of [Pd(η^4-C$_5$Me$_5$H)(η^5-C$_5$Me$_5$)]$^+$BF$_4^-$ (3)

Cerium(IV) ammonium nitrate (0.21 g, 0.38 mmol) was added to a solution of 3 (0.09 g, 0.19 mmol) and NaBF$_4$ (0.04 g, 0.38 mmol) in acetone (25 cm^3), and the mixture was stirred 0.5 h at room temperature. The solvent was removed in vacuo, and the residue washed with CH$_2$Cl$_2$ (3 × 10 cm^3), dissolved in water (5 cm^3) and filtered. An aqueous solution of NH$_4$PF$_6$ was added to the filtrate, to give a precipitate that was filtered off, washed with water, crystallized from CH$_2$Cl$_2$–Et$_2$O and dried in vacuo. Yield of 5, 0.05 g (38%). Anal. Found: C, 36.6; H, 4.5. C$_{20}$H$_{30}$F$_{12}$P$_2$Pd Calc.: C, 36.0; H, 4.5%. MS (FAB): m/z 522 [Pd(η^5-C$_5$Me$_5$)$_2$(PF$_6$)]; 377 [Pd(η^5-C$_5$Me$_5$)$_2$]. ^{1}H NMR (acetone-d_6): δ 2.32 (s, C$_5$Me$_5$) ppm. ^{13}C NMR (acetone-d_6): δ 9.3 (C$_5$Me$_5$); 123.5 (C$_5$Me$_5$) ppm.

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