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Novel β-iminoenolato (or β-carbonyliminato) complexes starting from di-μ-hydroxo palladium or platinum complexes with dimethyl acetylenedicarboxylate and primary amines: Crystal structure of $[NBu_4][(C_6F_5)_2Pd\{N(C_6H_4OMe\text{-}p)C(CO_2Me)CHC(O)OMe\}]$

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Abstract

The reaction of the binuclear hydroxo complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (M = Pd or Pt) with alkyl or arylamines (RNH_2) in the presence of dimethyl acetylenedicarboxylate (DMAD) yields the novel complexes $[NBu_4][(C_6F_5)_2M\{N(R)C(CO_2Me)CHC(O)\text{-}OMe\}]$ (M = Pd, R = C_6H_5 (**1**), *p*-MeC_6H_4 (**2**), *p*-$MeOC_6H_4$ (**3**), *p*-ClC_6H_4 (**4**), Et (**5**), Pr (**6**), $C_6H_5CH_2$ (**7**); M = Pt, R-*p*-MeC_6H_4 (**8**), *p*-$MeOC_6H_4$ (**9**)). Similar reactions carried out with $[PdR(PPh_3)(\mu\text{-}OH)]_2$ yield the complexes $[(PPh_3)RPd\{N(R')C(CO_2Me)CHC(O)OMe\}]$ (R = C_6F_5, R' = Me (**10**), Et (**11**), Pr (**12**), $CH_2C_6H_5$ (**13**); R = C_6H_5, R' = Me (**14**), Et (**15**), Pr (**16**), $CH_2C_6H_5$ (**17**)). However, the reaction of $[Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)]_2$ with $PhNH_2$ and DMAD yields $[Pd(C_6F_5)(PPh_3)]_2(\mu\text{-}OH)(\mu\text{-}NHPh)]$. The iminoenolate complex $[(PPh_3)(C_6F_5)Pd\{N(Ph)C(CO_2Me)CHC(O)OMe\}]$ (**18**) is obtained when the di-μ-hydroxo complex is treated with $HN(Ph)C(CO_2Me)CHC(O)OMe$. Protonation of complex **1** by HCl(aq) gives $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ and dimethyl *N*-phenyl-aminofumarate. $[NBu_4][(C_6F_5)_2Pd\{N(Ph)C(CO_2Me)CH_2C(O)O\}]$ (**19**) is obtained when complex **1** is treated with aqueous methanol. Conductivity measurements and spectroscopic (IR, ^1H, ^{13}C, ^{19}F and ^{31}P) methods have been used to characterize the complexes. The X-ray diffraction study of $[NBu_4][(C_6F_5)_2Pd\{N(C_6H_4OMe\text{-}p)C(CO_2Me)CHC(O)OMe\}]$ (**3**) has established that the coordination about palladium is approximately square planar and that there is substantial delocalization in the iminoenolate ligand.

Keywords: Palladium; X-ray crystal structure; μ-Hydroxo complexes; Dimethylacetylenedicarboxylate; Synthesis

1. Introduction

The 1,4 addition of amines to dimethyl acetylenedicarboxylate (DMAD) gives [1] cis–trans mixtures of the so-called Michael-type adducts $RHNC(CO_2Me)CH\text{-}CO_2Me$ which serve as intermediates for the synthesis of a variety of nitrogen-containing heterocyclic systems *via* oxidation with lead tetraacetate [2].

Insertion reactions under very mild conditions of DMAD with palladium amide complexes result in carbon–nitrogen bond formation [3]. For example, *trans*-$[Pd(C_6H_5)(NHPh)(PMe_3)_2]$ gives *trans*-$[Pd(C_6H_5)\text{-}\{C(CO_2Me)C(CO_2Me)NHPh\}(PMe_3)_2]$ where the deprotonated *N*-phenyl-aminomaleate ligand acts as an anionic monodentate C-donor ligand. The insertion of DMAD into an iridium–OH bond to afford the corresponding enol complex has been reported recently [4] and the ester-derived palladium enolate $[LPd\{Ph_2PCH{=}C(O)OEt\}]$ also reacts with DMAD to yield the alkenyl complex $[LPd\{Ph_2PCH[C(O)OEt](MeO_2CC{=}CCO_2Me)\}]$ [5]. Reactions of cyclopalladated complexes with acetylenes are also known, but these reactions proceed by insertion of the acetylene into the metal–carbon bond rather than the metal–nitrogen bond [6,7].

In the course of our investigations into hydroxo complexes of the nickel group elements, we have found

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that arylamines (RNH_2) react with the binuclear hydroxo complex $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ to give the amide complexes $[\{Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}OH)(\mu\text{-}NHR)]$ [8]. Binuclear amide complexes of the types $[\{Pd(C_6F_5)(^tBuNC)(\mu\text{-}NHR)\}_2]$ [8] and $[\{Pd(8\text{-}mq)_2(\mu\text{-}O_2CMe)(\mu\text{-}NHR)\}]$ [9] (8-mq = 8-quinolylmethyl) have also been prepared. We also know [10] that di-μ-amide complexes $[\{M(C_6F_5)_2(\mu\text{-}NHR)\}_2]^{2-}$ can be prepared by reaction of the the di-μ-hydroxo complexes $[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Pd or Pt) with arylamines. No reaction was, however, observed when it was attempted to react these arylamide-bridged complexes with DMAD in tetrahydrofuran, and the unreacted amide complex was recovered. In contrast, when the di-μ-hydroxo complexes are reacted with alkyl or arylamines in the presence of DMAD, the novel complexes $[NBu_4][(C_6F_5)_2M\{N(R)C(CO_2Me)CHC(O)OMe\}]$ (M = Pd or Pt) and $[(PPh_3)RPd\{N(R')C(CO_2Me)CHC(O)OMe\}]$ ($R = C_6F_5$ or C_6H_5) are obtained. This paper deals with the synthesis and structural characterization of these complexes.

2. Experimental details

The C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyser. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5°C min^{-1} and the solid samples under nitrogen flow (100 ml min^{-1}). Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Crison 525 conductimeter. The ^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ $CFCl_3$ or H_3PO_4 as standards respectively. Infrared spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. Solvents were dried by the usual methods. The starting complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (M = Pd [11], Pt [12]) and $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$ ($R = C_6F_5$ [13] or C_6H_5 [14]) were prepared by procedures described elsewhere.

2.1. $[NBu_4][(C_6F_5)_2Pd\{N(R)C(CO_2Me)CHC(O)OME\}]$ ($R = C_6H_5$ (1), C_6H_4Me-p (2), C_6H_4OMe-p (3), C_6H_4Cl-p (4), Et (5), Pr (6), $CH_2C_6H_5$ (7))

To a solution of $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (100 mg, 0.071 mmol) in tetrahydrofuran (5 ml) was added the corresponding amine RNH_2 (0.142 mmol) and DMAD (0.142 mmol). The resulting solution was stirred at room temperature for 4 h and the solvent was evaporated under vacuum. The residue was extracted with isopropanol–hexane and the white solid was collected by filtration, washed with hexane and air-dried. Complexes 1–7 were recrystallized from CH_2Cl_2–hexane.

2.2. $[NBu_4][(C_6F_5)_2Pt\{N(R)C(CO_2Me)CHC(O)OMe\}]$ ($R = C_6H_4Me$-p (8), C_6H_4OMe-p (9))

To a solution of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (100 mg, 0.063 mmol) in toluene (8 ml) was added the corresponding amine (0.378 mmol) and DMAD (0.378 mmol). After the solution was boiled under reflux for 8 h, the solvent was removed under vacuum and the white residue was extracted with isopropanol–hexane, then separated by filtration, washed with hexane and air-dried. Purification was achieved by recrystallization from dichloromethane–hexane.

2.3. $[(PPh_3)(C_6F_5)Pd\{N(R)C(CO_2Me)CHC(O)OMe\}]$ ($R = Me$ (10), Et (11), Pr (12), $CH_2C_6H_5$ (13))

To a solution of $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (90 mg, 0.0814 mmol) in tetrahydrofuran (6 ml) was added the corresponding amine (0.1628 mmol) and DMAD (0.1628 mmol). The resulting solution was stirred at room temperature for 4 h and the solvent was removed under vacuum. The residue was treated with hexane, with constant stirring, and then the solvent was removed under vacuum. Finally, the residue was treated with methanol to give a pale yellow precipitate, which was collected by filtration and air-dried.

2.4. $[(PPh_3)(C_6H_5)Pd\{N(R)C(CO_2Me)CHC(O)OMe\}]$ ($R = Me$ (14), Et (15), Pr (16), $CH_2C_6H_5$ (17))

To a solution of $[\{Pd(C_6H_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (90 mg, 0.0974 mmol) in tetrahydrofuran (6 ml) was added the corresponding amine (0.1948 mmol) and DMAD (0.1948 mmol). The resulting solution was stirred at room temperature for 4 h and then taken to dryness under vacuum. The residue was stirred under hexane for a few minutes and the solvent was then removed under vacuum. The residue was treated with isopropanol and a white solid was separated by filtration and air-dried.

2.5. Reaction of $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ with aniline and DMAD

To a solution of the hydroxo complex (100 mg; 0.0905 mmol) in tetrahydrofuran (8 ml) was added $PhNH_2$ (0.1810 mmol) and DMAD (0.1810 mmol) and the resulting solution was boiled under reflux for 7 h. The solvent was then eliminated under reduced pressure and methanol was added to the residue. A yellow precipitate was recovered by filtration and air-dried (yield 75%). The analytical and NMR (^1H, ^{19}F and ^{31}P) data identified the solid as the previously reported [8] μ-hydroxo-μ-amide complex *trans*-$[\{Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}OH)(\mu\text{-}NHPh)]$.

2.6. $[(PPh_3)(C_6F_5)\overline{Pd\{N(Ph)C(CO_2Me)CHC(O)OMe\}}]$ (18)

To a solution of dimethyl *N*-phenylamino fumarate $MeO_2CCH{=}C(NHPh)CO_2Me$ (prepared by addition of DMAD (0.181 mmol) to a solution of aniline (0.181 mmol) in diethyl ether (10 ml) with constant stirring for 14 h, and elimination of the solvent under reduced pressure) in methanol (6 ml) was added $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (100 mg, 0.0905 mmol). The solution was stirred at room temperature for 1 h during which time a yellow precipitate formed which was collected by filtration and air-dried.

2.7. Reaction of $[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with $MeO_2CCH{=}C(NHPh)CO_2Me$

A solution of $(NBu_4)_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (100 mg; 0.0714 mmol) and $MeO_2CCH{=}C(NHPh)CO_2Me$ (0.1428 mmol; prepared as described above) in tetrahydrofuran (8 ml) was stirred at room temperature for 4 h. After evaporation of the solvent under reduced pressure, the residue was treated with isopropanol and a white solid was collected by filtration and air-dried (yield 78%). This solid was identified as complex **1** by ^1H and ^{19}F spectroscopy.

2.8. Reaction of complex 1 with HCl(aq)

To a solution of **1** (400 mg, 0.437 mmol) in acetone (15 ml) was added HCl(aq) (0.437 mmol). After stirring the solution at room temperature for 30 min, the solvent was removed under vacuum and the residue was treated with diethyl ether. A white solid, identified as the known [15] di-μ-chloride palladium complex $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}Cl)\}_2]$, was filtered off, and acetone–dichloromethane was then added to the filtrate which was passed through a small column filled with florisil. On evaporation of the volatiles under vacuum, an oily residue resulted which was characterized [1] by ^1H NMR and ^{13}C NMR as dimethyl *N*-aminofumarate, $C_6H_5NHC(CO_2Me){=}CHCO_2Me$ (^1H NMR, in $CDCl_3$ δ (ppm) at 9.59 (brs, 1H, NH), 7.21, 7.03 and 7.05 (5 H, C_6H_5N), 5.32 (s, 1H, CH), 3.67 and 3.62 (ss, 6H, MeO); $^{13}C\{^1H\}$NMR, δ (ppm) 169.9 and 164.9 (CO_2Me), 148.0 and 140.2 (*C*–NHPh and C_{ipso} of Ph), 129.1, 124.2 and 120.6 (CH of Ph), 93.5 (=CH), 52.8 and 51.2 (MeO)).

M = Pd,	R =	C_6H_5	1
		p-MeC_6H_4	2
		p-$MeOC_6H_4$	3
		p-ClC_6H_4	4
		Et	5
		Pr	6
		$C_6H_5CH_2$	7
M = Pt,	R =	p-MeC_6H_4	8
		p-$MeOC_6H_4$	9

Scheme 1.

Table 1
Crystal structure determination details

Crystal data	
Formula	$C_{41}H_{50}F_{10}N_2O_5Pd$
Fw	947.3
Crystal system	orthorhombic
Space group	*Pbca* (No. 61)
Cell dimensions	
a (Å)	15.648(6)
b (Å)	20.099(3)
c (Å)	28.019(7)
α (deg)	90
β (deg)	90
γ (deg)	90
Cell volume (Å^3)	8812
Z	8
D_{calc} (g cm^{-3})	1.43
F(000)	3888
Monochromated Mo Kα radiation	
λ (Å)	0.71069
μ (cm^{-1})	5.0
Temperature (K)	293
Data collection	
Crystal size (mm^3)	0.3×0.25×0.2
Diffractometer	Enraf–Nonius CAD4
No. of reflections for calculating cell; θ_{min}, θ_{max}, (deg)	
Scan mode for data collection	θ–2θ
Data reflection ranges: θ min and max (deg)	*h* 0 → 18, *k* 0 → 23, 0 → 23, *l* 0 → 33; 2 → 25
Total unique reflections measured	8467
No. of significant reflections, $\lvert F^2\rvert > 2\sigma(F^2)$ [a]	4118
Max change in standard reflections (%)	−0.2
Decay correction	no
Empirical absorption correction, T_{max}, T_{min}	0.999, 0.954
Structure solution and refinement	
Non-H atoms located by	heavy atom methods SHELXS-86
Refinement by	full matrix least squares non-H atoms anisotropic Enraf–Nonius MolEN programs
Hydrogen atoms	fixed calculated positions $U_{iso} = 1.3\ U_{eq}$ for parent atom
R	0.056
R'	0.055
S	1.2
No. of variables	532
No. of reflections used in the refinement	4118
Max (Δ/σ)	0.02
Max, min (Δ/ρ) (e Å^{-3})	+0.43, −0.16

[a] $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, $w = \sigma^{-2}(F)$, $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ minimized.

2.9. Reaction of complex 1 with methanol

A suspension of complex **1** (100 mg; 0.109 mmol) in methanol (10 ml) was stirred at room temperature for 7 h to give a clear solution. After complete evaporation of the solvent under reduced pressure, the residue was treated with isopropanol and the solid was collected by filtration and air-dried. This white solid was identified as $[NBu_4][(C_6F_5)_2Pd\{N(Ph)C(CO_2Me)CH_2C(O)O\}]$ (**19**).

2.10. X-ray structure determination

A crystal of **3** suitable for a diffraction study was grown from dichloromethane–hexane. Details of data collection and refinement are given in Table 1. Additional material available from the authors or the Cambridge Crystallographic Data Centre comprises tables of intramolecular distances and angles, hydrogen atom coordinates, anisotropic temperature factors, and least squares planes for **3** (10 pages).

3. Results and discussion

The preparations of $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OH)_2\}_2]$ (M = Pd [11] or Pt [12]) and their reactions with weak protic acids were previously reported. Both hydroxo complexes react with primary amines RNH_2 (two equivalents for Pd or an excess for Pt) in the presence of DMAD (two equivalents for Pd or an excess for Pt) in tetrahydrofuran either at room temperature (Pd) or boiling under reflux (Pt) to give the complexes $[NBu_4][(C_6F_5)_2M\{N(R)C(CO_2Me)CHC(O)OMe\}]$ **1–9** shown in Scheme 1.

The analytical data (Table 2) for complexes **1–9** were consistent with the proposed formulae, and in acetone solution they behave as 1:1 electrolytes [16]. The IR spectra of these bis(pentafluorphenyl) derivatives show the characteristic absorptions of the C_6F_5 group [17] at 1630, 1490, 1450, 1050, 950 and a split band at ca. 800 cm^{-1}. This latter is derived from the so-called X-sensitive mode in C_6F_5–halogen molecules, which is characteristic of the *cis*-$Pd(C_6F_5)_2$ fragment [18] and behaves like a ν(M–C) band [19]. A strong absorption observed at ca. 1730 cm^{-1} is assigned to the uncoordinated CO_2Me group and two bands at ca. 1590 and 1515 cm^{-1} are the combination bands ν(CC) + ν(CO) and ν(CO) + ν(CC) respectively.

The ^1H NMR spectra of these complexes (Table 3) show the presence of a singlet at *ca.* 4.2 ppm assigned to the CH proton and two singlets at ca. 3.4 and 3.2 ppm for the methoxy protons. The observation of three or two signals for the aromatic protons of the arylamide groups indicates that rotation of the aryl group about the C–N bond is rapid on the NMR time scale. The ^{19}F NMR spectra indicate the presence of two different types of C_6F_5 group freely rotating about the carbon–metal bond; each C_6F_5 group gives the three expected signals (relative intensities of 2:1:2) for the *ortho*-, *para*- and *meta*-fluorine atoms respectively, although overlapping of some signals is observed in some instances. The $^{13}C\{^1H\}$ NMR spectrum of **3** in Me_2CO-d_6 shows the two carboxyl peaks at 169.5 and 167.8 ppm, a peak for the CH group at 75.6, and three peaks for the methoxy carbons at 55.4, 51.1 and 50.9 ppm. The

Table 2
Analytical data, yields and physical properties for complexes 1–9

Complex	Yield (%)	M.p. [a] (°C)	Analysis (%) [b]			Selected IR bands [c]			Λ_M [d]
			C	H	N	ν(C=O)	ν(CC) + ν(CO), ν(CO) + ν(CC)	ν(M–C_6F_5)	
1	68	230	52.1 (52.4)	5.2 (5.3)	2.9 (3.1)	1730	1600, 1520	790, 780	100
2	71	227	52.7 (52.9)	5.7 (5.4)	2.9 (3.1)	1730	1595, 1520	795, 780	99
3	73	230	51.8 (52.0)	5.5 (5.3)	2.9 (3.0)	1730	1595, 1520	795, 780	95
4	75	227	50.2 (50.5)	5.1 (5.0)	2.9 (2.9)	1730	1600, 1520	795, 780	99
5	73	220	49.5 (49.8)	5.6 (5.6)	3.1 (3.2)	1745	1590, 1535	790, 780	101
6	71	231	49.8 (50.3)	5.9 (5.7)	3.1 (3.2)	1720	1590, 1525	795, 780	99
7	75	183	52.5 (52.9)	5.4 (5.4)	3.0 (3.0)	1730	1595, 1515	795, 780	102
8	73	231	47.9 (48.3)	4.8 (4.9)	2.7 (2.8)	1730	1590, 1525	810, 795	97
9	74	232	47.5 (47.5)	5.0 (4.9)	2.6 (2.7)	1730	1590, 1525	810, 795	100

[a] With decomposition. [b] Calculated values in parentheses. [c] In Nujol mulls (cm^{-1}). [d] S cm^2 mol^{-1} (in acetone)

Table 3
NMR spectroscopic data [a,b] (J in Hz) for complexes 1–9

Complex	^1H [c]	^{19}F
1	6.45(dd, 2 H_m, $J_{om} = J_{mp}$ 7.4)	−114.4 (d, 2 F_o, J_{om} 29.4)
	6.22 (t, 1 H_p, J_{mp} 7.4)	−115.2(d, 2 F_o, J_{om} 30.5)
	6.62 (d, 2 H_o, J_{om} 7.4)	−165.4(t, 1 F_p, J_{mp} 19.8)
	4.29 (s, 1 H, CH)	−166.6 (m, 2 F_m + 1 F_p)
	3.42 (s, 3 H, CO_2Me)	−167.2 (m, 2 F_m)
	3.21 (s, 3 H, CO_2Me)	
2	6.87(d, 2 H_o, J_{om} 7.8)	−114.3 (d, 2 F_o, J_{om} 29.1)
	6.46 (d, 2 H_m, J_{om} 7.8)	−115.1 (d, 2 F_o, J_{om} 29.6)
	4.26 (s, 1 H, CH)	−165.4 (t, 1 F_o, J_{mp} 19.8)
	3.41 (s, 3 H, CO_2Me)	−166.7 (m, 2 F_m)
	3.24 (s, 3 H, CO_2Me)	−167.1 (t, 1 F_o, J_{mp} 19.2)
	2.07 (s, 3H, *p*-Me)	−167.5 (m, 2 F_m)
3	6.52 (d, 2 H_o, J_{om} 8.0)	−114.3 (d, 2 F_o, J_{om} 29.9)
	6.38 (d, 2 H_m, J_{om} 8.0)	−115.1 (d, 2 F_o, J_{om} 29.9)
	4.25 (s, 1 H, CH)	−165.3 (t, 1 F_o, J_{mp} 19.8)
	3.68 (s, 3 H, *p*-MeO)	−166.7 (m, 2 F_m + 1 F_p)
	3.40 (s, 3 H, CO_2Me)	−167.1 (m, 2 F_m)
	3.25 (s, 3 H, CO_2Me)	
4	6.83 (d, 2 H_o, J_{om} 8.6)	−114.4 (d, 2 F_o, J_{om} 29.4)
	6.59 (d, 2 H_m, J_{om} 8.6)	−115.4 (d, 2 F_o, J_{om} 29.4)
	4.33(s, 1 H, CH)	−165.1 (t, 1 F_p, J_{mp} 19.8)
	3.42 (s, 3 H, CO_2Me)	−166.1 (t, 1 F_p, J_{mp} 19.8)
	3.28 (s, 3 H, CO_2Me)	−167.0 (m, 4 F_m)
5	3.97 (s, 1 H, CH)	−113.1 (d, 2 F_o, J_{om} 29.4)
	3.71 (s, 3 H, CO_2Me)	−115.7 (d, 2 F_o, J_{om} 29.9)
	3.31 (s, 3 H, CO_2Me)	−165.1 (t, 1 F_p, J_{mp} 19.8)
	2.81 (m, 2 H, NCH_2)	−165.5 (t, 1 F_p, J_{mp} 19.8)
	0.82 (t, 2 H, NCH_2CH_3, J 6.9)	−166.3 (m, 2 F_m)
		−166.7 (m, 2 F_m)
6	3.97 (s, 1 H, CH)	−113.2 (d, 2 F_o, J_{om} 29.4)
	3.69 (s, 3 H, CO_2Me)	−115.7 (d, 2 F_o, J_{om} 29.9)
	3.31 (s, 3 H, CO_2Me)	−165.3 (t, 1 F_p, J_{mp} 19.5)
	2.66 (m, 2 H, NCH_2)	−165.4 (t, 1 F_p, J_{mp} 19.5)
	1.42 (m, 2 H, NCH_2CH_2)	−166.4 (m, 2 F_m)
	0.35 (t, 3 H, CH_2CH_3, J 6.9)	−166.7 (m, 2 F_m)
7	7.09(dd, 2 H_m, $J_{om} = J_{mp}$ 7.4)	−113.6 (d, 2 F_o, J_{om} 29.4)
	7.04 (t, 1 H_p, J_{mp} 7.4)	−115.2 (d, 2 F_o, J_{om} 30.2)
	6.89 (d, 2 H_o, J_{om} 7.4)	−165.4 (t, 1 F_p, J_{mp} 19.5)
	4.18 (s, 2 H, NCH_2)	−165.9 (t, 1 F_p, J_{mp} 19.8)
	4.11 (s, 1 H, CH)	−166.9 (m, 4 F_m)
	3.21 (s, 3 H, CO_2Me)	
	3.42 (s, 3 H, CO_2Me)	
8	6.64 (d, 2 H_o, J_{om} 7.8)	−117.7 (d, 2 F_o, J_{om} 26.2, J_{PtF_o} 536.2)
	6.53 (d, 2 H_m, J_{om} 7.8)	−119.1 (d, 2 F_o, J_{om} 26.5, J_{PtF_o} 445.9)
	4.36 (s, 1 H, CH)	−167.0 (t, 1 F_p, J_{mp} 19.2)
	3.46 (s, 3 H, CO_2Me)	−167.9 (m, 2 F_m)
	3.25 (s, 3 H, CO_2Me)	−169.1 (m, 1 F_p + 2 F_m)
	2.10 (s, 3 H, *p*-Me)	
9	6.57 (d, 2 H_o, J_{om} 8.7)	−117.7 (d, 2 F_o, J_{om} 28.2, J_{PtF_o} 536.2)
	6.41 (d, 2 H_m, J_{om} 8.7)	−119.0 (d, 2 F_o, J_{om} 29.9, J_{PtF_o} 443.1)
	4.36 (s, 1 H, CH)	−167.1 (t, 1 F_p, J_{mp} 19.8)
	3.60 (s, 3 H, *p*-MeO)	−168.0 (m, 2 F_m)
	3.46 (s, 3 H, CO_2Me)	−168.8 (m, 2 F_m + 1 F_p)
	3.27 (s, 3 H, CO_2Me)	

[a] Chemical shifts in ppm from TMS (^1H) or from $CFCl_3$ (^{19}F). Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] In $(CD_3)_2CO$. [c] Additional peaks of $[NBu_4]^+$ are found at ca. 3.43 (t, NCH_2), 1.80 (m, NCH_2CH_2), 1.40 (m, CH_2CH_3) and 0.95 (t, CH_3), the relative intensities being 8:8:8:12 respectively.

attempted ^{15}N NMR spectrum of **3** by the INEPT technique confirmed that there is no proton on the nitrogen atom. We have recently demonstrated that in the reaction of amines with the hydroxo complexes $[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Ni [20], Pd, Pt [21]) in the presence of carbon disulphide, C–N bonds are formed to give *N*,*N*-dialkyldithiocarbamate complexes. In these reactions, and also in that of the DMAD, the nucleophilic attack of the RNH^- ion, generated in situ by deprotonation of the amine by the hydroxo complex, on the unsaturated organic system gives the anionic ligand to be bonded to the metal centre. The alternative route of the direct addition of the amine to DMAD and deprotonation of the RNH group of the resulting dimethyl *N*-arylaminofumarate is also possible [22].

The structure of **3** in the solid state has been determined by a single-crystal X-ray diffraction study. Fractional atomic coordinates and selected bond distances and bond angles are presented in Tables 4 and 5 respectively and the molecular structure of the anion of complex **3** is shown in Fig. 1. Coordination at palladium is approximately square planar, with slight buckling. The six-membered chelate ring is close to planar and careful examination of the bond lengths reveals substantial delocalization. Relatively few N–O chelates of palladium of this type are available for comparison, and these structures are all complicated by the fact that the ligands are in fact tetradentate with additional amino coordinating groups. The bond lengths in the chelate ring vary, with examples in which the C–C bonds of the chelate are similar in length [23–25] lying between a double and a single bond, as obtained here. However, in [Pd(baden)]NCS (baden = 1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-O,*N*,*N*′,*N*″) more double bond localization occurs [24]. The Pd–N and Pd–O bonds are somewhat longer in **3** than in the related examples, which may be attributed to the steric demands of the C_6F_5 ligands. Both the uncoordinated ester group and the 4-methoxyphenyl group are twisted

Table 4
Fractional atomic coordinates and equivalent isotropic thermal parameters

	x	y	z	U_{eq}
Pd	0.22979(3)	0.08451(3)	0.12703(2)	0.041(1)
F1	0.1985(3)	−0.0421(2)	0.1911(1)	0.067(3)
F2	0.0686(3)	−0.1266(2)	0.1959(2)	0.087(3)
F3	−0.0750(3)	−0.1055(2)	0.1444(2)	0.104(4)
F4	−0.0853(3)	0.0026(3)	0.0862(2)	0.109(4)
F5	0.0452(3)	0.0873(2)	0.0800(2)	0.087(3)
F6	0.1906(3)	0.0939(2)	0.2392(1)	0.074(3)
F7	0.1207(3)	0.1892(3)	0.2918(1)	0.094(3)
F8	0.0653(3)	0.3030(2)	0.2507(2)	0.094(3)
F9	0.0757(3)	0.3174(2)	0.1544(2)	0.097(3)
F10	0.1423(3)	0.2218(2)	0.1009(1)	0.080(3)
O1	0.3990(3)	−0.0252(3)	−0.0077(2)	0.062(3)
O2	0.4383(3)	−0.0788(2)	0.0586(2)	0.053(3)
O3	0.4715(3)	0.1735(2)	0.1083(2)	0.060(3)
O4	0.1088(4)	−0.2073(3)	0.0201(2)	0.106(5)
O5	0.3363(3)	0.1472(2)	0.1235(2)	0.051(3)
N1	0.2897(3)	0.0156(2)	0.0833(2)	0.041(3)
N2	0.6495(3)	−0.0517(3)	0.1478(2)	0.045(3)
C1	0.3685(4)	0.0227(3)	0.0683(2)	0.040(4)
C2	0.4243(4)	0.0741(3)	0.0785(2)	0.042(4)
C3	0.4046(4)	0.1315(3)	0.1044(2)	0.042(4)
C4	0.4581(5)	0.2334(4)	0.1342(3)	0.076(6)
C5	0.4031(4)	−0.0290(3)	0.0346(2)	0.047(4)
C6	0.4587(5)	−0.1375(4)	0.0315(3)	0.071(5)
C7	0.2440(4)	−0.0414(3)	0.0666(2)	0.042(4)
C8	0.1846(5)	−0.0354(3)	0.0306(3)	0.057(5)
C9	0.1375(5)	−0.0890(4)	0.0144(3)	0.068(5)
C10	0.1512(5)	−0.1512(4)	0.0338(3)	0.065(5)
C11	0.2108(5)	−0.1581(3)	0.0697(3)	0.066(5)
C12	0.2566(5)	−0.1036(3)	0.0864(3)	0.055(5)
C13	0.0389(8)	−0.2001(5)	−0.0085(6)	0.244(12)
C14	0.1276(4)	0.0268(3)	0.1358(2)	0.040(4)
C15	0.1289(4)	−0.0277(4)	0.1642(2)	0.047(4)
C16	0.0624(5)	−0.0729(4)	0.1670(3)	0.059(5)
C17	−0.008(5)	−0.0630(4)	0.1414(3)	0.059(5)
C18	−0.0136(5)	−0.0089(4)	0.1132(3)	0.063(5)
C19	0.0538(5)	0.0352(4)	0.1101(3)	0.056(5)
C20	0.1710(4)	0.1530(3)	0.1675(2)	0.041(4)
C21	0.1618(4)	0.1484(3)	0.2160(2)	0.047(4)
C22	0.1268(5)	0.1971(4)	0.2442(3)	0.060(5)
C23	0.0976(5)	0.2543(4)	0.2233(3)	0.061(5)
C24	0.1048(5)	0.2606(4)	0.1755(3)	0.060(5)
C25	0.1394(5)	0.2108(4)	0.1486(2)	0.052(4)
C26	0.6847(5)	−0.0995(4)	0.1844(2)	0.056(5)
C27	0.6400(5)	−0.1649(4)	0.1891(3)	0.068(5)
C28	0.6861(6)	−0.2105(4)	0.2224(3)	0.091(6)
C29	0.6430(7)	−0.2753(5)	0.2313(44)	0.119(8)
C30	0.7048(4)	0.0100(4)	0.1495(3)	0.056(5)
C31	0.6821(6)	0.0653(4)	0.1159(3)	0.073(6)
C32	0.7452(6)	0.1218(4)	0.1201(3)	0.089(6)
C33	0.7229(7)	0.1811(5)	0.0902(4)	0.124(8)
C34	0.5570(5)	−0.0349(4)	0.1584(2)	0.052(4)
C35	0.5389(5)	−0.0012(4)	0.2057(3)	0.076(6)
C36	0.4425(6)	0.0081(5)	0.2110(3)	0.108(7)
C37	0.4157(9)	0.0402(7)	0.2515(5)	0.201(12)
C38	0.6494(4)	−0.0827(4)	0.0975(2)	0.051(4)
C39	0.7337(5)	−0.1062(4)	0.0789(3)	0.064(5)
C40	0.7224(6)	−0.1391(4)	0.0312(3)	0.072(5)
C41	0.8044(7)	−0.1641(5)	0.0098(3)	0.109(7)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Selected intramolecular distances (Å) and angles (deg) for 3, with estimated standard deviations in parentheses

Bonds			
Pd–O5	2.091(4)	Pd–C20	2.007(6)
Pd–C14	1.991(6)	O2–C5	1.326(8)
O1–C5	1.189(8)	O3–C3	1.350(8)
O2–C6	1.438(9)	O5–C3	1.237(8)
O3–C4	1.421(9)	C2–C3	1.396(9)
C1–C2	1.382(9)	C1–C5	1.505(9)
Pd–N1	2.074(5)	N1–C1	1.310(8)
Angles			
O5–Pd–N1	90.8(2)	O5–Pd–C14	175.5(2)
O5–Pd–C20	88.8(2)	N1–Pd–C14	92.7(2)
N1–Pd–C20	178.1(2)	C14–Pd–C20	87.8(3)
Pd–O5–C3	123.8(4)	Pd–N1–C1	122.7(4)
O5–C3–C2	128.8(6)	C1–C2–C3	125.8(6)
N1–C1–C2	127.7(6)		

out of the plane of the chelate ring, to alleviate crowding.

There are a number of examples of *cis*-$Pd(C_6F_5)_2$ units in complexes of which the structures have been determined. The Pd–C14 bond (1.991(6) Å) is quite similar to that trans to oxygen in $[NBu_4][\{Pd(C_6F_5)_2(acac)\}_2\mu Ag]$ [26] (1.985(6) and 1.990(6) Å). The Pd–C20 bond (2.007(6) Å) is comparable with that in *cis*-$[NBu_4][Pd(C_6F_5)_2(pyrazole)(pyrazolate)]$ [18] (2.007(5) Å). These values are in accord with the expected trans-influence of the N/O ligand but, given the standard deviations observed, it may be unwise to attach too much significance to them. The CPdC angle (87.8(3)°) is at the low end of the range typical for $\{Pd(C_6F_5)_2\}$ units, perhaps because of the steric effect of the N–aryl group.

The neutral di-μ-hydroxo complexes $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5 or C_6H_5) also react with primary alkyl amines $R'NH_2$ (two equivalents) in the presence of DMAD (two equivalents) in tetrahydrofuran, at room

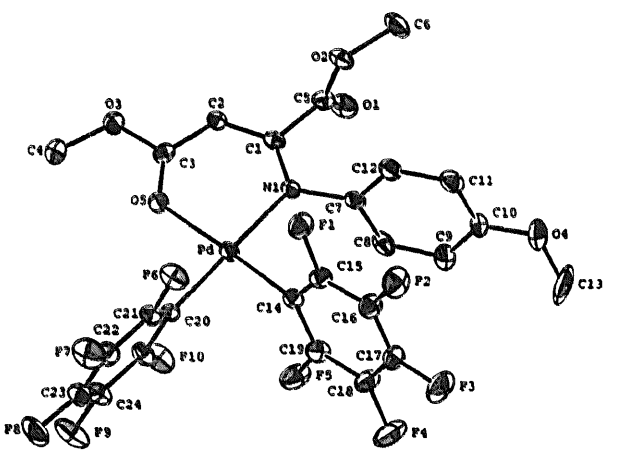
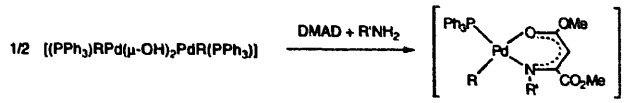


Fig. 1. Molecular structure of the anion of complex 3. The ORTEP diagram shows the non-H atoms as 20% thermal vibration ellipsoids.

temperature, to give the corresponding β-iminoenolate complexes **10–17** (Scheme 2). These complexes behave as non-electrolytes in acetone solution. The IR spectra show the presence of the C_6F_5 group and only a single band for the 'X-sensitive mode' of C_6F_5 (Table 6).

The ^{1}H NMR spectra of these neutral complexes (Table 7) show three singlets at ca. 4.2 (CH), 3.7 and 2.6 (methoxy protons). The doublet signals observed for the NMe protons of complexes **10** and **14** and the NCH_2Ph protons of **13** and **17** are caused by coupling to the P atom of the phosphine ligand, and, for the same reason, the NCH_2Me (for **11** and **15**) and NCH_2Et (for **12** and **16**) resonances are observed as multiplet signals. All this suggests that the phosphine ligand is trans to the N atom of the β-iminoenolate ligand, as shown in Scheme 2. As expected, three signals with relative intensities of 2:1:2 are found in the ^{19}F NMR spectra of complexes **10–13** and one singlet in the ^{31}P{^{1}H} NMR spectra.

It is worth mentioning that the neutral β-iminoenolate complexes **10–17** are all derived from alkyl amines. The reaction of *trans*-[{Pd(C_6F_5)(PPh_3)(μ-OH)}$_2$] with the arylamine aniline and DMAD gives the previously reported μ-hydroxo-μ-anilido complex *trans*-[{Pd(C_6F_5)(PPh_3)}$_2$(μ-OH)(μ-NHPh)] instead of the β-iminoenolate complex. This result shows that for the more acidic aniline the acid–base reaction $\rangle$Pd(μ-OH)$_2$Pd$\langle$ + $PhNH_2$ → $\rangle$Pd(μ-OH)(μ-NHPh)$\langle$ + H_2O is faster than the addition reaction with the DMAD to give



R = C_6F_5, R' =	Me	10
	Et	11
	Pr	12
	$C_6H_5CH_2$	13
R = C_6H_5, R' =	Me	14
	Et	15
	Pr	16
	$C_6H_5CH_2$	17

Scheme 2.

the $PhNH_2$–DMAD adduct. The π-acceptor character of the PPh_3 ligand should also enhance the basicity of the bis(hydroxo) complex. Nevertheless, the iminoenolate complex **18** could be prepared by reacting the bis(μ-hydroxo) complex with $MeO_2CC(NHPh)CHCO_2$Me (Scheme 3).

The reaction of [{Pd(C_6F_5)$_2$(μ-OH)}$_2$]$^{2-}$ with $MeO_2CC(NHPh)CHCO_2$Me was also studied and, as expected, complex **1** was the reaction product. The reaction of complex **1** with HCl(aq) in 1:1 molar ratio in acetone afforded (Scheme 3) the previously reported [15] di-μ-chloride palladium complex [NBu_4]$_2$[(C_6F_5)$_2$Pd(μ-Cl)$_2$Pd(C_6F_5)$_2$] and the enamine dimethyl *N*-phenylamino fumarate, characterized by ^{1}H and ^{13}C NMR (see Experimental section). It has been reported that the addition of aniline to DMAD in benzene gives an 80:20 mixture of aminomaleate–aminofumarate

Table 6
Analytical data, yields and physical properties for complexes **10–19**

Complex	Yield (%)	M.p. [a] (°C)	Analysis (%) [b]			Selected IR bands [c]			Λ_M [d]
			C	H	N	ν(C=O)	ν(CC) + ν(CO), ν(CO) + ν(CC)	ν(M-C_6F_5)	
10	77	215	52.4 (52.6)	3.6 (3.6)	2.0 (2.0)	1740	1590, 1515	800	
11	80	201	52.9 (53.2)	3.7 (3.8)	1.8 (1.9)	1735	1590, 1515	800	
12	79	197	53.7 (53.9)	4.0 (4.0)	1.9 (1.9)	1735	1590, 1515	800	
13	75	204	56.4 (56.7)	3.6 (3.7)	1.7 (1.8)	1730	1590, 1515	800	
14	72	184	60.2 (60.3)	4.9 (4.9)	2.2 (2.3)	1740	1595, 1515		
15	75	186	60.8 (60.8)	5.2 (5.1)	2.0 (2.2)	1725	1595, 1510		
16	78	184	61.6 (61.4)	5.4 (5.3)	2.1 (2.2)	1725	1595, 1515		
17	79	178	63.6 (64.0)	5.0 (4.9)	2.0 (2.0)	1730	1600, 1515		
18	82	232	56.0 (56.1)	3.4 (3.5)	1.7 (1.8)	1738	1584, 1518	800	
19	80	204	51.8 (51.8)	5.2 (5.1)	3.1 (3.1)	1740	1650 [e], 1644 [e]	798, 788	95

[a] With decomposition. [b] Calculated values in parentheses. [c] In Nujol mulls (cm^{-1}). [d] S cm^2 mol^{-1} (in acetone). [e] ν(CO) of C(O)O–Pd.

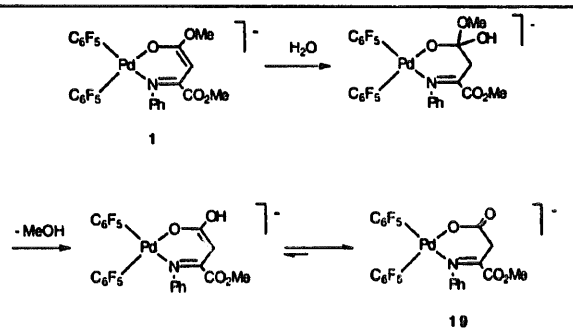
Table 7
NMR data (J in Hz) for complexes **10–19** (in $CDCl_3$)

Complex	^1H δ($SiMe_4$)	^{19}F δ($CFCl_3$)	^{31}P δ (H_3PO_4)
10	7.50 (m, 6 H_o, PPh_3) 7.43 (m, 3 H_p, PPh_3) 7.37 (m, 6 H_m, PPh_3) 4.18 (s, 1 H, CH) 3.72 (s, 3 H, CO_2Me) 2.60 (d, 3 H, NMe, J_{PH} 1.9) 2.55 (s, 3 H, CO_2Me)	−118.4 (d, 2 F_o, J_{om} 21.2) −161.1 (t, 1 F_p, J_{mp} 19.8) −162.6 (m, 2 F_m)	27.8 (s)
11	7.51 (m, 6 H_o, PPh_3) 7.37 (m, 3 H_p, PPh_3) 7.27 (m, 6 H_m, PPh_3) 4.13 (s, 1 H, CH) 3.72 (s, 3 H, CO_2Me) 2.78 (m, 2 H, NCH_2) 2.52 (s, 3 H, CO_2Me) 0.79 (t, 3 H, NCH_2CH_3, J_{HH} 7.2)	−116.8 (d, 2 F_o, J_{om} 21.2) −161.0 (t, 1 F_p, J_{mp} 19.8) −162.6 (m, 2 F_m)	27.8 (s)
12	7.51 (m, 6 H_o, PPh_3) 7.30 (m, 3 H_p, PPh_3) 7.37 (m, 6 H_m, PPh_3) 4.13 (s, 1 H, CH) 3.72 (s, 3 H, CO_2Me) 2.63 (m, 2 H, NCH_2) 2.53 (s, 3 H, CO_2Me) 1.32 (m, 2 H, NCH_2CH_2) 0.39 (t, 3 H, CH_2CH_3, J_{HH} 7.3)	−116.9 (d, 2 F_o, J_{om} 21.2) −161.2 (t, 1 F_p, J_{mp} 19.8) −162.7 (m, 2 F_m)	28.6 (s)
13	7.44 (m, 6H_o, PPh_3) 7.32 (m, 3 H_p, PPh_3) 7.23 (m, 6 H_m, PPh_3) 7.06 (m, 2 H_o + 1 H_p, $C_6H_5CH_2$) 6.75 (d, 2 H_m, $C_6H_5CH_2$, J 6.9) 4.26 (s, 1 H, CH) 4.18 (d, 2 H, NCH_2, J_{HH} 3.3) 3.57 (s, 3 H, CO_2Me) 2.57 (s, 3 H, CO_2Me)	−117.9 (d, 2 F_o, J_{om} 21.2) −161.9 (t, 1 F_p, J_{mp} 19.8) −163.8 (m, 2 F_m)	28.0 (s)
14	7.24 (m, 15 H, PPh_3) 6.98 (d, 2 H_o, C_6H_5Pd, J 7.2) 6.58 (m, 2 H_m + 1 H_p, C_6H_5Pd) 4.12 (s, 1 H, CH) 3.68 (s, 3 H, CO_2Me) 2.56 (s, 3 H, CO_2Me) 2.42 (d, 3 H, NMe, J_{PH} 1.9)		29.8 (s)
15	7.24 (m, 15 H, PPh_3) 6.99 (d, 2 H_o, C_6H_5Pd, J 7.2) 6.55 (m, 2 H_m + 1 H_p, C_6H_5Pd) 4.12 (s, 1 H, CH) 3.68 (s, 3 H, CO_2Me) 2.67 (m, 2H, NCH_2) 2.53 (s, 3H, CO_2Me) 0.76 (t, 3 H, NCH_2CH_3, J_{HH} 7.0)		29.8 (s)
16	7.24 (m, 15 H, PPh_3) 6.99 (d, 2 H_o, C_6H_5Pd, J 7.2) 6.55 (m, 2 H_m + 1 Hp, C_6H_5Pd) 4.04 (s, 1 H, CH) 3.67 (s, 3 H, CO_2Me) 2.53 (s, 3 H, CO_2Me) 2.50 (m, 2 H, NCH_2) 1.30 (m, 2 H, NCH_2CH_2) 0.18 (t, 3 H, CH_2CH_3, J_{HH} 7.3)		29.8 (s)

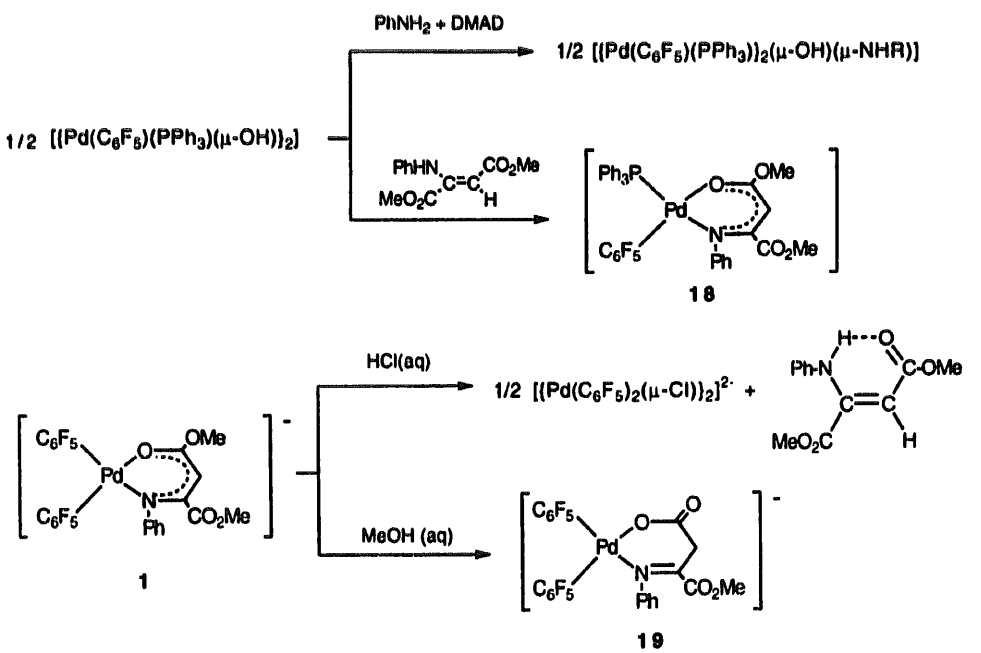
Table 7 (continued)

Complex	^1H δ(SiMe$_4$)	^{19}F δ(CFCl$_3$)	^{31}P δ (H$_3$PO$_4$)
17	7.22 (m, 15 H, PPh$_3$) 6.99 (d, 2 H$_o$, C$_6$H$_5$Pd, *J* 7.2) 7.06 (m, 2 H$_o$ + 1 Hp, C$_6$H$_5$CH$_2$) 4.19 (s, 1 H, CH) 3.96 (d, 2 H, NCH$_2$, J_{HH} 2.4) 3.48 (s, 3 H, CO$_2$Me) 2.60 (s, 3 H, CO$_2$Me)		30.0 (s)
18	7.52 (m, 6 H$_o$, PPh$_3$) 7.32 (m, 6 H$_m$ + 3 H$_p$, PPh$_3$) 6.75 (m, 5 H, NC$_6$H$_5$) 4.47 (s, 1 H, CH) 3.26 (s, 3 H, CO$_2$Me) 2.71 (s, 3 H, CO$_2$Me)	−119.1 (d, 2 F$_o$, J_{om} 22.85) −162.5 (t, 1 F$_p$, J_{mp} 20.04) −164.1 (m, 2 F$_m$)	28.7 (s)
19	7.05 (m, 2 H$_m$ + 1 Hp, NPh) 6.70 (d, 2 H$_o$, J_{om} 6.75) 3.62 (s, 3 H, CO$_2$Me) 3.41 (s, 2 H, CH$_2$)	−114.9 (d, 2 F$_o$, J_{om} 22.85) −116.9 (d, 2 F$_o$, J_{om} 22.85) −162.7 (t, 1 F$_p$, J_{mp} 19.75) −163.3 (t, 1 F$_p$, J_{mp} 21.45) −164.9 (m, 2 F$_m$) −165.6 (m, 2 F$_m$)	

which gives on standing (23 h) the thermodynamically stable isomer (the aminofumarate) [27]. However, when complex **1** was treated with aqueous methanol at room temperature complex **19** was obtained (Scheme 3). The formation of complex **19** requires the hydroxy-de-alkoxylation of coordinated N(Ph)C(CO$_2$Me)CHC(OMe)O–, i.e., an addition–elimination process on a C=C double bond [28]. The suggested mechanism is presented in Scheme 4 where the anionic organic ligand in complex **1** is represented by its iminoenolate form.



Scheme 4.



Scheme 3.

Acknowledgements

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