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Addition of arenediazonium ligands to a Pd–Pd bond: a reinvestigation

Francesco Neve*, Marcello Longeri, Mauro Ghedini and Alessandra Crispini
Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS) (Italy)

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Abstract

Arenediazonium salts [p-$YC_6H_4N_2$][BF_4] (Y = H, CH_3, OCH_3, F, NO_2) react with the A-frame precursor complexes [Pd_2X_2(dppm)$_2$] (**1**) (X = Cl, Br, I; dppm = bis(diphenylphosphino)methane) affording 1:1 adducts. ^1H and ^{31}P NMR spectroscopic data support the formulation of the new complexes as A-frame molecules [Pd_2X_2(dppm)$_2$(μ-N_2-p-C_6H_4Y)][BF_4] (**2**) containing a symmetrically bridging arenediazenido ligand. The crystal structures of [Pd_2I_2(dppm)$_2$(μ-N_2-p-$C_6H_4CH_3$)][BF_4] (**2d**) and [Pd_2Cl_2(dppm)$_2$(μ-N_2-p-C_6H_4F)][BF_4] (**2f**) have been determined by X-ray crystallography. **2d** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z=4$ in a unit cell of dimensions $a=14.642(4)$, $b=19.166(5)$, $c=21.338(6)$ Å. The structure was refined to $R=0.068$ and $R_w=0.073$ on the basis of 4325 observed reflections with $I>3\sigma(I)$. **2f** crystallizes in the tetragonal space group $P\bar{4}_32_12$ with $a=14.886(1)$, $c=25.303(8)$ Å and $Z=4$. The structure was refined to $R=0.039$ and $R_w=0.043$ using 4681 unique reflections and 353 parameters. The formation of [$PtPdCl_2$(dppm)$_2$(μ-N_2-p-C_6H_4F)][BF_4] (**4**) and its solution structure is also described.

Introduction

The ligands NO^+ and RNN^+ are isoelectronic and this analogy can be used for synthetic purposes [1–3]. The bimetallic species [M_2Cl_2(dppm)$_2$] (M = Pd, Pt; dppm = bis(diphenylphosphino)methane) contain a metal–metal bond and the nitrosonium ion NO^+ can easily insert into it [4], with formation of stable products only in the platinum case. On the other hand, arenediazonium salts react with [Pt_2Cl_2(dppm)$_2$] in a similar way to give highly stable and robust diazenido species [5].

In 1978 Rattray and Sutton made a brief report on the reactivity of [Pd_2Cl_2(dppm)$_2$] with several o- and p-substituted arenediazonium salts [6]. In their experimental work they observed the formation of complexes of general formula [Pd_2Cl_2(dppm)$_2$(N_2Ar)]X (X = BF_4 or PF_6). On the basis of analytical and conductivity data alone they established the stoichiometry of the formed species. They also suggested the presence of a bridging arenediazenido ligand by inspection of the ^{31}P NMR spectra which were not however reported.

We therefore decided to reinvestigate this chemistry using [Pd_2X_2(dppm)$_2$] (X = Cl, Br, I) (**1**) as precursors and p-substituted arenediazonium tetrafluoroborate salts. We report here on the synthesis and complete structural characterization of the reaction products [Pd_2X_2(dppm)$_2$(μ-N_2-p-C_6H_4Y)][BF_4] (**2**) both in solution and in solid state. In any case the complexes herein described are all different from Sutton's ones except for the chloro derivative of p-fluorobenzenediazonium ligand (**2f**). The reactivity of the mixed-metal species [$PtPdCl_2$(dppm)$_2$] (**3**) with [p-$FC_6H_4N_2$][BF_4] is also reported for comparison.

Experimental

General data

All reactions were carried out under a nitrogen atmosphere in dried solvents. Bis(diphenylphosphino)methane (Aldrich), p-nitro and p-methoxybenzenediazonium tetrafluoroborate salts (Aldrich) were commercially available. p-Fluorobenzenediazonium, p-methylbenzenediazonium and benzenediazonium tetrafluoroborate salts were synthesized by a published procedure [7]. [Pd_2X_2(dppm)$_2$] (X = Cl (**1a**), Br (**1b**), I (**1c**)) [8], and [$PdPtCl_2$(dppm)$_2$] (**3**) [9] were prepared according to literature methods.

NMR spectra were obtained at 300 (^1H) or 121.5 (^{31}P) MHz on a Bruker AC 300 spectrometer. Chemical shifts (in ppm) are referenced to internal Me_4Si (^1H) and to external 85% H_3PO_4 (^{31}P). The $^{31}P\{^1H\}$ FID of **2e** was transferred to a Bull-Zenith PC and then trans-

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*Author to whom correspondence should be addressed.

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formed and phased with Bruker's WIN-NMR software. The file containing the phased spectrum was then transferred to a Digital 3100 VAX station where it was analyzed in terms of six spectral parameters (*C2v* symmetry) using the DAVSYM simulation/iteration program [10]. The spectrum manipulating routine (SPECPREP) was slightly modified in the baseline correction, noise flattening, and spectrum display routines. Only the sum $|^2J(P_AP_{A'}) - {}^2J(P_BP_{B'})|$ was found according to that reported for similar spin systems [11].

Electronic spectra were recorded on a Hitachi U-2000 spectrophotometer. IR spectra were obtained on a Perkin-Elmer 1330 instrument. Microanalyses were performed by the Microanalytical Laboratory of our department.

Preparation of compounds

[Pd$_2$Cl$_2$(dppm)$_2$(μ-N$_2$C$_6$H$_5$)][BF$_4$] (2a)

A solution of [$C_6H_5N_2$][BF_4] (90.7 mg, 0.48 mmol) in acetone (5 ml) was added by cannula to a stirred suspension of **1a** (100 mg, 0.095 mmol) in acetone (10 ml). The resulting red–orange solution was stirred for 30 min. The solvent was then removed by a rotary evaporator, and the residue partially redissolved in dichloromethane. The solid unreacted benzenediazonium salt was filtered off, and diethyl ether slowly added to the filtrate to give a red microcrystalline solid. Yield 97 mg (82%). *Anal.* Calc. for $C_{56}H_{49}BCl_2F_4N_2P_4Pd_2$: C, 54.09; H, 3.97; N, 2.25. Found: C, 53.95; H, 3.84; N, 2.30%. Λ_m (acetone, 25 °C, 1×10^{-4} M): 142.1 Ω^{-1} M^{-1} cm^2.

The complexes **2b–i** were prepared in a similar way using the appropriate [Pd_2X_2(dppm)$_2$] precursor. The color, yield, equivalent conductance and analytical data for **2b–i** are as follows.

2b: red–orange, 50%, 156.5 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{57}H_{51}BCl_2F_4N_2P_4Pd_2$: C, 54.40; H, 4.09; N, 2.23. Found: C, 54.75; H, 3.97; N, 1.95%.

2c: red, 85%, 136.4 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{57}H_{51}BBr_2F_4N_2P_4Pd_2$: C, 50.81; H, 3.81; N, 2.08. Found: C, 50.40; H, 3.90; N, 1.93%.

2d: dark red, 90%, 171.2 $\Omega - 1$ M^{-1} cm^2. *Anal.* Calc. for $C_{57}H_{51}BF_4I_2N_2P_4Pd_2$: C, 47.49; H, 3.56; N, 1.94. Found: C, 46.35; H, 3.52; N, 2.22%.

2e: orange, 77%, 136.8 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{57}H_{51}BCl_2F_4N_2OP_4Pd_2$: C, 53.71; H, 4.03; N, 2.20. Found: C, 52.45; H, 3.94; N, 2.15%.

2f: orange, 76%, 140.3 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{56}H_{48}BCl_2F_5N_2P_4Pd_2$: C, 53.88; H, 3.87; N, 2.24. Found: C, 53.35; H, 3.71; N, 2.23%.

2g: red–orange, 90%, 153.0 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{56}H_{48}BBr_2F_5N_2P_4Pd_2$:C, 49.68; H, 3.37; N, 2.20. Found: C, 50.30; H, 3.62; N, 2.09%.

2h: red, 78%, 150.6 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{56}H_{48}BF_5I_2N_2P_4Pd_2$:C, 46.99; H, 3.38; N, 1.96. Found: C, 46.30; H, 3.26; N, 2.10%.

2i: red–orange, 87%, 137.4 Ω^{-1} M^{-1} cm^2. *Anal.* Calc. for $C_{56}H_{48}BCl_2F_4N_3O_2P_4Pd_2$:C, 52.20; H, 3.75; N, 3.26. Found: C, 51.81; H, 3.74; N, 3.11%.

[PtPdCl$_2$(dppm)$_2$(μ-N$_2$-p-C$_6$H$_4$F)][BF$_4$] (4)

A suspension of **3** (150 mg, 0.131 mmol) in acetone (10 ml) was treated with [*p*-$FC_6H_4N_2$][BF_4] (60 mg, 0.66 mmol) dissolved in acetone (15 ml). A dark orange solution was obtained after 15 min stirring. Stirring was continued for an additional 45 min, then the solvent was evaporated to dryness and the desired orange product was obtained as above described for **2a**. Yield 139 mg (79%). *Anal.* Calc. for $C_{56}H_{48}BCl_2F_5N_2O_2P_4PdPt$: C, 50.30; H, 3.62; N, 2.10. Found: C, 48.88; H, 3.42; N, 2.27%.

X-ray crystallography

Crystal data for complexes **2d** and **2f** are summarized in Table 1. Both structures were solved by standard heavy-atom methods and Fourier techniques. Refinement of the structures was carried out by full-matrix least-squares methods.

All calculations were performed with the Siemens SHELXTL PLUS [12] and PARST [13] programs. Atomic scattering factors and anomalous dispersion terms were those supplied in the Siemens structure determination package.

[Pd$_2$I$_2$(dppm)$_2$(μ-N$_2$-p-C$_6$H$_4$CH$_3$][BF$_4$]·0.75CH$_2$Cl$_2$ (2d)

All observed intensities were corrected for absorption using a semi-empirical method [14]. Calculated transmission factors ranged from 0.448 to 0.687 based on $\mu = 18.35$ cm^{-1}. The Pd, I, P, N(1) and methylenic-C atoms were anisotropically refined and the remaining non-hydrogen atoms were refined with isotropic thermal parameters. The phenyl ring of the arenediazenido ligand was constrained to a rigid group with C−C bond distances of 1.395 Å and D_{6h} symmetry. The phenyl hydrogen atoms were not included in the refinement. All the remaining hydrogen atoms were added in their idealized position (d(C−H) = 0.96 Å) with their isotropic thermal parameters set at $U = 0.08$ Å^2. Three fluorine atoms of the BF_4^- anion are disordered in two positions and their site-occupation factors were fixed at 0.5. The additional peaks shown in the final difference map (2.6–1.08 e/Å^3) are assigned to a solvent molecule of CH_2Cl_2. This molecule was refined with calculated occupancy factors of 0.75. During the refinement the chlorine atoms appeared to be badly disordered and the hydrogen atoms were not included

TABLE 1. Crystallographic data for $[Pd_2I_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)][BF_4]$ (**2d**) and $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**2f**)

	2d	**2f**
Formula	$C_{57}H_{51}BF_4I_2N_2P_4Pd_2\cdot 0.75CH_2Cl_2$	$C_{56}H_{48}BCl_2F_5N_2P_4Pd_2$
Formula weight	1503.5	1262.4
Crystal system	orthorhombic	tetragonal
Space group	$P2_12_12_1$ (No. 19)	$P4_32_12$ (No. 96)
a (Å)	14.642(4)	14.886(1)
b (Å)	19.166(5)	
c (Å)	21.338(6)	25.303(8)
V (Å^3)	5988(3)	5607(2)
Z	4	4
Crystal size (mm)	0.52×0.14×0.12	0.35×0.22×0.40
ρ_{calc} (g cm^{-3})	1.668	1.495
Temperature (°C)	22±2	22±2
λ (Å)	0.71073	0.71073
μ(Mo Kα) (cm^{-1})	18.35	8.94
Scan method	ω	ω
Scan speed (° min^{-1})	2.0–15.0	2.0–15.0
Diffractometer	Siemens R3m/V	Siemens R3m/V
2θ Range (°)	3.0–50.0	3.0–52.0
Octants collected	$-h, k, -l$	$h, k, -l$
No. data	5871	6153
No. unique data	5841	5557
No. observed data ($6\sigma(F_o)$)	4325	4681
No. variables	357	353
N_o/N_v	12.1	13.3
R^a	0.068	0.039
$R_w{}^b$	0.073	0.043
GOF^c	1.19	1.23
q Factor	0.004	0.001
Δ/σ (mean)	0.072	0.018
Δ/ρ (e Å^{-3})	1.20	1.23

[a] $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o{}^2]^{1/2}$; $w^{-1}=\sigma(F_o)^2+q(F_o)^2$. [c] Goodness of fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$.

owing to the large thermal parameters of the carbon atom.

$[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (2f)

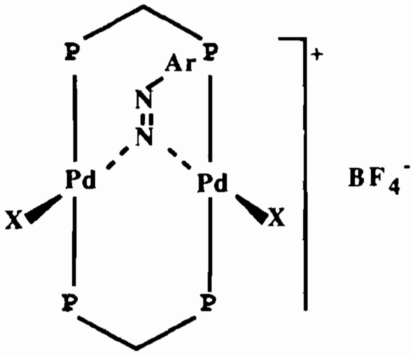
The systematic absences and the Laue symmetry (4/*mmm*) indicated either the space group $P4_32_12$ or the enantiomorphic $P4_12_12$. The structure was solved in the space group $P4_32_12$. In the final stage the Pd, Cl, P, N, F(1) and all carbon atoms were refined with anisotropic thermal parameters and the atoms of the BF_4^- anion were refined isotropically. The hydrogen atoms were fixed in the idealized position and refined with a common thermal parameter ($U=0.08$ Å^2). Convergence was achieved with the final values $R=0.0394$ and $R_w=0.0426$. Although parallel refinement was carried out in the enantiomorphic space group $P4_12_12$, the initial choice giving slightly better agreement factors (R and R_w ratios were 1.046 and 1.026, respectively) was maintained. No absorption correction was applied to the intensity data.

The final atomic positional and thermal parameters for compounds **2d** and **2f** are listed in Tables 2 and 3.

Results and discussion

Arenediazonium salts $[p\text{-}YC_6H_4N_2][BF_4]$ (Y=H, CH_3, OCH_3, F, NO_2) insert into the metal–metal bond of $[Pd_2X_2(dppm)_2]$ (**1**) to give the stable cationic species $[Pd_2X_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4Y)][BF_4]$ (**2**). Whereas Sutton's procedure was followed for the choice of solvent and reaction temperature, we observed that the use of only one mole equivalent of diazonium salt would afford a much longer reaction time and lower yields. A five-fold molar excess was then used in all preparations.

Compounds **2a–i** are orange or red air-stable solids whose electronic spectral parameters are reported in Table 4. Analytical and conductivity data confirmed the expected stoichiometry, which was substantiated by a thorough ^{1}H and ^{31}P NMR investigation. ^{1}H NMR spectra of **2a–i** can be divided into two distinct spectral regions. The first one, 6.5–8.5 ppm, containing aromatic proton resonances due to phenyl groups of dppm and arenediazenido ligands, is of negligible interest. The other one, 2.0–3.0 ppm, with dppm methylene proton resonances, is structurally significative. The signals observed in this region are indeed characteristic of A-



	X	Y
2a	Cl	H
2b	Cl	CH_3
2c	Br	CH_3
2d	I	CH_3
2e	Cl	OCH_3
2f	Cl	F
2g	Br	F
2h	I	F
2i	Cl	NO_2

frame structures [5, 15]. The inequivalent methylene protons give rise to AB doublets showing further splittings due to coupling with a tightly coupled P_4 sub spin system (Fig. 1). No further evidences on the type of the phosphorus sub spin system were evinced from the proton spectra. In **2a–i** the highfield proton signals show the larger $^1H–^{31}P$ coupling as opposed to several palladium(II) dppm A-frames [15–17].

The ^{31}P NMR spectra of **2a–i** reveal the presence of two dissimilar types of phosphorus atoms, as earlier observed by Rattray and Sutton [6]. At room temperature an AA′BB′ pattern can be seen and in the case of **2e** the resolution was good enough to allow 18 of the expected 24 lines [18] to be observed (Fig. 2(b)). The analysis of the spectrum of **2e** gave the parameters reported in Table 5.

The mixed-metal species $[PdPtCl_2(dppm)_2]$ (**3**) irreversibly reacts with $[p\text{-}FC_6H_4N_2][BF_4]$ to give insertion of the arenediazonium ligand into the Pd–Pt bond. The product, $[PtPdCl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**4**), is present in solution as a mixture of two different stereoisomers. The two isomers (**A** and **B**) probably result from differing orientations of the phenyl ring at the diazenido nitrogen atom not involved in coordination to the metals. The isomeric ratio, as deduced from NMR spectra, is approximately 2:1 and does not change if a longer reaction time is used.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for complex **2d**

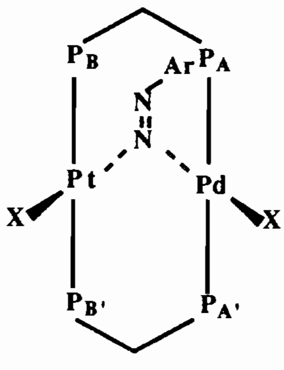
	x	*y*	*z*	U_{eq}[a]
Pd(1)	9330(1)	9041(1)	112(1)	30(1)
Pd(2)	10409(1)	9739(1)	−1077(1)	30(1)
I(1)	7934(1)	8353(1)	530(1)	67(1)
I(2)	10518(1)	9916(1)	−2288(1)	53(1)
P(1)	10297(3)	8065(2)	85(2)	31(1)
P(2)	8464(3)	10072(2)	82(2)	36(1)
P(3)	11125(3)	8650(2)	−1167(2)	29(1)
P(4)	9726(4)	10829(2)	−884(2)	38(1)
C(1)	11338(11)	8256(9)	−378(8)	34(5)
C(2)	9149(13)	10822(8)	−109(9)	38(5)
N(1)	10410(10)	9617(7)	−139(6)	37(4)
N(2)	10985(8)	9831(6)	180(5)	19(2)
C(3)	11106(12)	9806(10)	816(6)	67(6)
C(4)	12008	9833	1026	82(8)
C(5)	12206	9719	1657	102(10)
C(6)	11502	9577	2079	83(8)
C(7)	10600	9550	1869	84(8)
C(8)	10402	9664	1238	81(8)
C(9)	11739(21)	9428(17)	2679(15)	89(9)
C(10)	10776(13)	7872(10)	851(8)	38(4)
C(11)	10193(15)	7908(12)	1386(10)	53(5)
C(12)	10496(19)	7670(15)	1982(12)	73(7)
C(13)	11435(20)	7556(16)	2000(14)	80(8)
C(14)	11982(20)	7541(15)	1563(13)	80(8)
C(15)	11694(18)	7721(14)	944(12)	68(7)
C(16)	9848(11)	7210(9)	−188(8)	30(4)
C(17)	9161(13)	7172(10)	−557(9)	42(4)
C(18)	8903(17)	6495(13)	−789(11)	62(6)
C(19)	9367(17)	5952(13)	−627(11)	64(6)
C(20)	10052(17)	5982(14)	−232(11)	63(6)
C(21)	10331(14)	6626(12)	6(9)	50(5)
C(22)	7930(13)	10347(10)	831(8)	40(4)
C(23)	7079(21)	10102(16)	942(13)	84(8)
C(24)	6612(21)	10260(17)	1513(14)	88(8)
C(25)	7133(23)	10679(17)	1915(15)	93(9)
C(26)	7923(21)	10857(16)	1835(13)	80(8)
C(27)	8412(15)	10708(12)	1264(10)	57(6)
C(28)	7540(13)	10037(10)	−466(8)	38(4)
C(29)	6962(14)	10644(11)	−518(9)	47(5)
C(30)	6241(20)	10603(17)	−967(14)	82(8)
C(31)	6089(21)	10048(17)	−1335(14)	88(8)
C(32)	6640(17)	9455(13)	−1296(11)	63(6)
C(33)	7378(14)	9494(12)	−854(9)	50(5)
C(34)	12242(13)	8661(10)	−1492(8)	40(4)
C(35)	13018(18)	8789(13)	−1145(11)	64(6)
C(36)	13900(20)	8824(15)	−1411(13)	77(8)
C(37)	13988(19)	8735(15)	−2039(13)	74(7)
C(38)	13286(18)	8618(14)	−2375(12)	69(7)
C(39)	12380(13)	8537(11)	−2146(9)	44(5)
C(40)	10515(11)	8001(9)	−1608(7)	30(4)
C(41)	9725(13)	8177(10)	−1911(9)	43(4)
C(42)	9252(16)	7643(13)	−2259(11)	61(6)
C(43)	9642(17)	7000(13)	−2309(11)	64(6)
C(44)	10444(17)	6821(12)	−2020(11)	62(6)
C(45)	10871(16)	7318(13)	−1651(11)	58(6)
C(46)	10594(14)	11495(10)	−827(9)	45(5)
C(47)	11340(14)	11447(11)	−1208(10)	51(5)
C(48)	12018(18)	11983(14)	−1201(12)	69(7)
C(49)	11910(21)	12476(16)	−791(14)	83(8)

(*continued*)

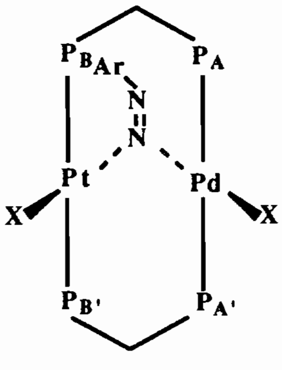
TABLE 2. (*continued*)

	x	y	z	U_{eq}[a]
C(50)	11201(26)	12534(20)	−451(17)	106(11)
C(51)	10596(24)	12028(18)	−409(15)	98(9)
C(52)	8830(13)	11168(10)	−1398(9)	42(4)
C(53)	8522(18)	11858(14)	−1293(12)	69(7)
C(54)	7836(22)	12123(18)	−1654(15)	93(9)
C(55)	7399(23)	11710(19)	−2135(15)	98(10)
C(56)	7679(18)	11028(15)	−2162(12)	71(7)
C(57)	8410(16)	10752(13)	−1814(11)	60(6)
B	9803(28)	2460(22)	1272(18)	87(10)
F(1)	9252(16)	2264(13)	754(10)	130(7)
F(2)	10431(34)	2831(27)	949(22)	139(15)
F(3)	9782(28)	1938(21)	1757(18)	111(12)
F(4)	9427(26)	3004(20)	1539(17)	101(10)
F(2a)	9108(31)	2323(25)	1653(20)	125(13)
F(3a)	10344(50)	1826(41)	1202(33)	213(28)
F(4a)	10310(48)	2786(38)	1630(31)	192(24)
C(58)	4174(66)	1106(51)	224(43)	211(35)
Cl(1)	3490(14)	587(12)	−367(10)	183(8)
Cl(2)	4060(27)	1161(21)	772(18)	289(16)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.



A



B

The presence of two different isomers in the ^{1}H NMR spectrum of **4** is apparent in the aromatic region wherein two sets of resonances at 8.38/8.29 and 6.66/6.64 ppm can be assigned to the protons *meta* and *ortho* to the fluoro substituent of the arenediazenido bridging ligand in the major and minor species, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of **4** shows the expected AA'BB' pattern with superimposed AA'BB'X component. The multiplet centred at 3.21 ppm is assigned to P_B belonging to the major isomer. The $^1J(PtP_B)$ value at 2900 Hz is similar to the value observed in $[Pt_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ [5], but smaller than that found for other A-frames derived from $[PdPtCl_2(dppm)_2]$ [9]. The P_A resonance can be seen downfield at 9.78 ppm. The phosphorus resonances for the minor isomer are at 6.68 and 7.78 ppm for P_B and P_A, respectively.

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3) for complex **2f**

	x	y	z	U_{eq}[a]
Pd(1)	1407(1)	7624(1)	7960(1)	34(1)
P(1)	2287(1)	8490(1)	8542(1)	37(1)
P(2)	365(1)	6980(1)	7389(1)	37(1)
Cl(1)	1528(1)	6314(1)	8450(1)	59(1)
N(1)	1302(3)	8698(3)	7500	39(2)
N(2)	727(3)	9273(3)	7500	53(2)
C(1)	2477(4)	9619(4)	8270(2)	39(2)
C(2)	41(7)	9490(8)	7818(5)	45(4)
C(3)	−135(9)	9053(9)	8289(5)	49(4)
C(4)	−882(9)	9330(11)	8596(5)	62(5)
C(5)	−1424(10)	10023(10)	8394(6)	64(5)
C(6)	−1232(10)	10460(10)	7925(8)	73(6)
C(7)	−520(10)	10190(9)	7655(6)	60(6)
C(8)	3387(4)	8081(5)	8747(2)	48(2)
C(9)	3955(5)	8630(7)	9036(3)	69(3)
C(10)	4787(6)	8283(9)	9188(3)	92(4)
C(11)	5045(6)	7436(9)	9062(4)	94(4)
C(12)	4473(7)	6919(6)	8779(4)	86(4)
C(13)	3643(5)	7228(5)	8612(3)	62(2)
C(14)	1666(4)	8725(4)	9148(2)	47(2)
C(15)	1824(6)	9505(6)	9451(3)	78(3)
C(16)	1360(8)	9614(8)	9907(3)	101(4)
C(17)	734(8)	9031(9)	10070(4)	105(5)
C(18)	571(9)	8321(8)	9800(5)	121(5)
C(19)	1047(7)	8157(6)	9332(4)	98(4)
C(20)	−723(4)	7218(5)	7667(2)	51(2)
C(21)	−1373(5)	7727(6)	7428(3)	77(3)
C(22)	−2159(7)	7906(10)	7689(4)	123(5)
C(23)	−2303(6)	7611(10)	8185(4)	111(5)
C(24)	−1671(6)	7093(9)	8433(3)	98(4)
C(25)	−894(5)	6896(6)	8172(3)	73(3)
C(26)	380(5)	5783(4)	7254(2)	46(2)
C(27)	1183(5)	5339(4)	7248(3)	58(2)
C(28)	1203(8)	4436(5)	7097(3)	82(3)
C(29)	427(10)	4013(5)	6963(4)	101(5)
C(30)	−372(8)	4441(7)	6984(4)	101(4)
C(31)	−415(6)	5351(5)	7119(3)	76(3)
F(1)	−2116(6)	10239(8)	8684(4)	103(5)
B	7326(78)	7326(78)	0	539(78)
F(2)	7736(18)	7119(17)	412(10)	222(10)
F(3)	7326(29)	8359(27)	163(14)	273(14)
F(4)	6904(20)	7498(20)	305(11)	246(10)
F(5)	8089(14)	8238(14)	280(7)	214(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Molecular structures

The structures of $[Pd_2I_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)][BF_4]$ (**2d**) and $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**2f**) have been determined by X-ray diffraction. Their cations are shown in Figs. 3 and 4 and selected bonding parameters are listed in Tables 6 and 7.

The most significant structural features of **2d** have been defined despite the somewhat large standard deviations. Severe disorder in the arenediazenido ligand is the most probable reason for the high value of the agreement factor. The cation of **2f** lie astride a crys-

TABLE 4. Electronic spectral data for $[Pd_2X_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4Y)][BF_4]$ (**2**) complexes[a]

Compound	λ_{max} (ϵ (cm^{-1} M^{-1}))
$[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2C_6H_5)][BF_4]$ (**2a**)	431(4708), 341(21595)
$[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)][BF_4]$ (**2b**)	432(3146), 347(17090)
$[Pd_2Br_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)][BF_4]$ (**2c**)	447(3584), 350(sh, 14686)
$[Pd_2I_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)][BF_4]$ (**2d**)	452(6429), 324(sh, 33154)
$[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)][BF_4]$ (**2e**)	433(3680), 357(24730)
$[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**2f**)	430(3975), 340(19740)
$[Pd_2Br_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**2g**)	441(3903), 366(10360)
$[Pd_2I_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**2h**)	453(7214), 312(sh, 36860)
$[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4NO_2)][BF_4]$ (**2i**)	427(2806), 341(16129)

[a] Dichloromethane solutions at 23 °C.

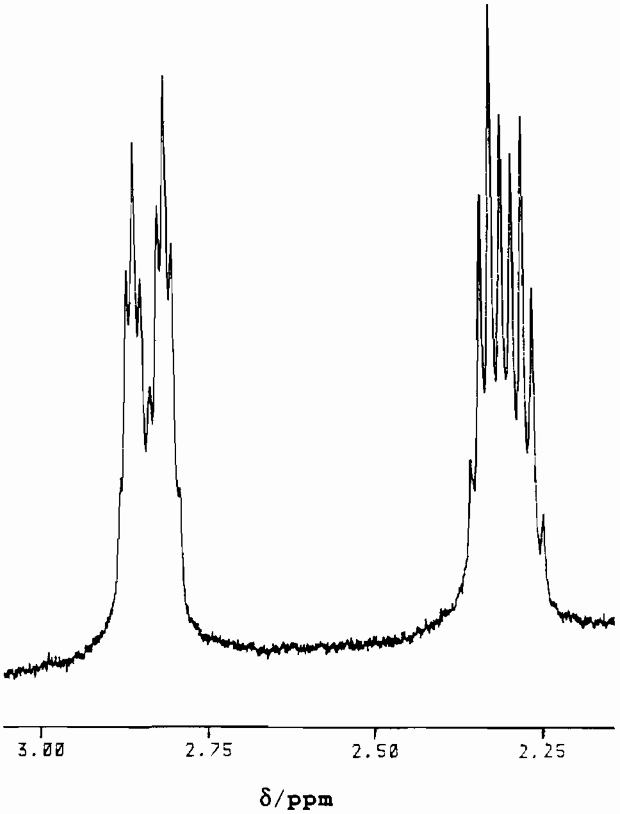


Fig. 1. ^1H NMR spectrum of **2f** in CD_2Cl_2 in the region of methylene protons.

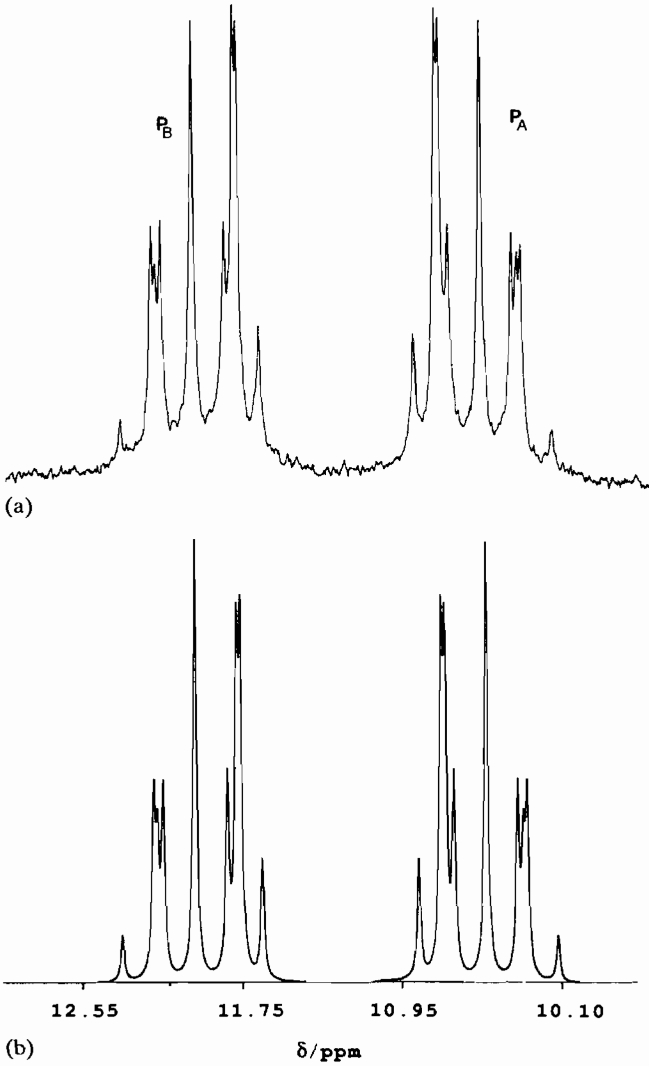


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of **2e** in CD_2Cl_2 at 20 °C and 121.5 MHz (a) and the simulated spectrum (b) using the parameters listed in Table 5.

tallographically imposed C_2 axis coincident with the N–N vector. Both cations have an overall A-frame geometry with bridging dppm and arenediazenido ligands. The Pd···Pd separation in **2d**, 3.274(2) Å, is well within the range reported for similar dinuclear palladium compounds [15, 19–22]. The corresponding distance at 3.096(1) Å in **2f** is however considerably shorter.

The two palladium(II) centres in **2d** and **2f** have a distorted square planar coordination geometry with regular Pd–P and Pd–halide bond distances. The angle between normals to the PdP_2XN mean planes is 64° in **2d** and 97.7° in **2f**. The methylene bridges of the dppm ligands are bent toward the arenediazenido bridging ligand affording the typical 'boat' conformation for the $Pd_2P_4C_2$ ring.

TABLE 5. ^{1}H and $^{31}P\{^{1}H\}$ NMR parameters[a]

Complex	$^{1}H^{b}$, CH_2 (dppm)			$^{31}P^{c}$
	δ	J(PH)	J(HH)	δ^{d}
2a[e]	2.76 2.26	2.9 4.5	13.9	11.02
2b[f]	2.81 2.28	3.0 4.5	13.8	11.38
2c[g]	2.71 2.33	2.9 4.6	13.8	11.50
2d[h]	2.60 2.38	2.8 4.4	13.5	11.63
2e[e, i]	2.65 2.24	nr nr	13.0	11.96[j] 10.52[j]
2f[e]	2.83 2.30	3.0 4.5	13.8	10.95
2g	2.76 2.37	3.1 4.5	13.9	11.15
2h	2.64 2.40	2.7 4.5	13.8	11.27
2i	2.88 2.58	nr 4.4	14.0	11.52
4	2.88[k] 2.47[k]	3.4 4.8	14.0	9.74[k, l, m] 3.21[k, l, m]
	2.86[n] 2.53[n]	nr 4.4	14.2	7.78[l, n, o] 6.68[l, n, o]

[a] δ in ppm, J in Hz; nr = not resolved. All spectra recorded at 20 °C. [b] In CD_2Cl_2 unless otherwise noted. $J(PH) = |^{2}J(PH) + {}^{4}J(PH)|$. [c] In CH_2Cl_2 (75%)/acetone-d_6 (25%). [d] Midpoint of AA'BB' pattern. [e] In $CDCl_2CDCl_2$. [f] $\delta(Ar{-}CH_3) = 2.16$ ppm. [g] $\delta(Ar{-}CH_3) = 2.20$ ppm. [h] $\delta(Ar{-}CH_3) = 2.25$ ppm. [i] $\delta(Ar{-}OCH_3) = 3.77$ ppm. [j] AA'BB' multiplet with $|^{2}J(P_AP_{A'}) - {}^{2}J(P_BP_{B'})| = 23.19$, $^{2}J(P_AP_B) = 56.47$ and $^{4}J(P_AP_{B'}) = -4.87$ Hz. [k] Major species. [l] AA'BB' multiplet with superimposed AA'BB'X component. [m] $^{1}J(PtP_A) = 2900$, $^{3}J(PtP_B) = 179$, $N = |^{2}J(P_AP_B) + {}^{4}J(P_AP_{B'})| = 38$ Hz. [n] Minor species. [o] $^{1}J(PtP_A) = 2946$, $^{3}J(PtP_B) = 175$, $N = |^{2}J(P_AP_B) + {}^{4}J(P_AP_{B'})| = 37$ Hz.

The arenediazenido ligand in **2d** and **2f** symmetrically bridges the two metal ions in a μ-η^{1} fashion. Bond distances within the N=NAr group are similar to the values reported for complexes wherein the ligand shows the same coordination mode [23–25]. The N=N distance of 1.16(2) Å in **2d** is however rather short and to some extent is a consequence of severe disorder at the N(2) position.

The bridgehead Pd–N–Pd angle at 109.2(7)° in **2d** is similar to the value observed in $[Pt_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4OCH_3)][BF_4]$ (111.4(12)°) [5], while the corresponding angle in **2f** is more acute (102.6(1)°).

Finally, it must be recalled that Sutton and co-workers [26] earlier mentioned the crystal structure determination of complex **2f**, but no structural data have been published yet.

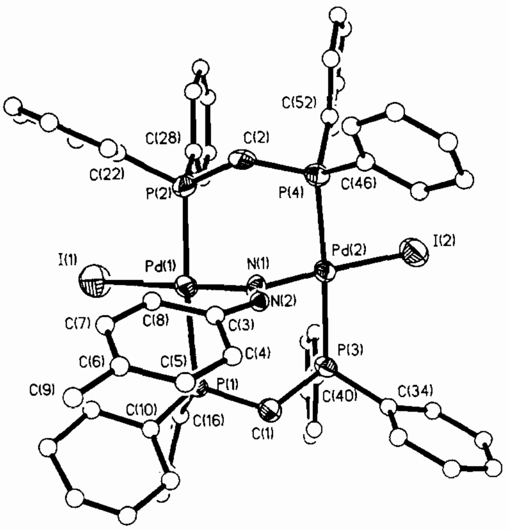


Fig. 3. Perspective view and atomic labeling scheme for the cation of $[Pd_2I_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4CH_3)][BF_4]$ (**2d**). The 50% probability ellipsoids are displayed, except for methyl and phenyl carbon atoms which are drawn with arbitrary radius spheres.

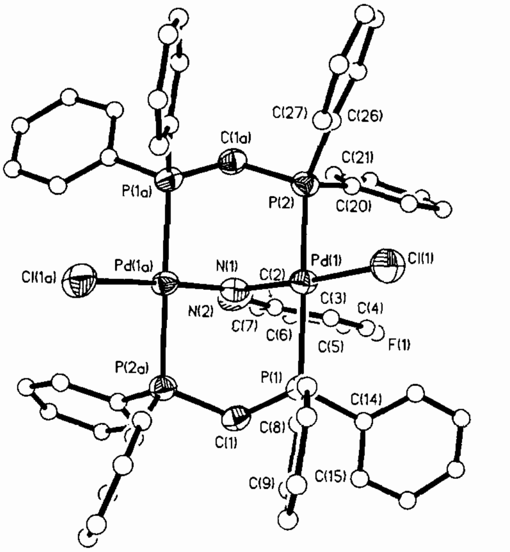


Fig. 4. Perspective view and atomic labeling scheme for the cation of $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)][BF_4]$ (**2f**). The 50% probability ellipsoids are displayed, except for fluorine and phenyl carbon atoms which are drawn with arbitrary radius spheres.

Conclusions

The characterization of the complexes of this study clearly indicates that predictions made by Rattray and Sutton [6] were correct. However some differences were observed in the stability and reactivity of the species.

Complexes **2** and **4** were found completely stable in dichloromethane solutions for weeks and partial decomposition was observed after days only in the case of iodo derivatives **2d** and **2h**. We also did not observe

TABLE 6. Selected bond parameters for **2d**

Bond distances (Å)			
Pd(1)–Pd(2)	3.274(2)	Pd(2)–P(3)	2.343(5)
Pd(1)–P(1)	2.346(5)	Pd(2)–P(4)	2.353(5)
Pd(1)–P(2)	2.350(5)	Pd(1)–N(1)	2.002(15)
Pd(1)–I(1)	2.590(2)	Pd(2)–N(1)	2.015(13)
Pd(2)–I(2)	2.612(2)	N(1)–N(2)	1.157(18)
N(2)–C(3)	1.37(2)	C(6)–C(9)	1.36(3)
Bond angles (°)			
P(1)–Pd(1)–P(2)	174.6(2)	P(3)–Pd(2)–P(4)	174.5(2)
I(1)–Pd(1)–N(1)	174.9(4)	I(2)–Pd(2)–N(1)	176.4(4)
P(1)–Pd(1)–N(1)	87.5(4)	P(3)–Pd(2)–N(1)	88.8(4)
P(2)–Pd(1)–N(1)	87.4(4)	P(4)–Pd(2)–N(1)	86.0(4)
P(1)–Pd(1)–I(1)	94.6(1)	P(3)–Pd(2)–I(2)	90.4(1)
P(2)–Pd(1)–I(1)	90.6(1)	P(4)–Pd(2)–I(2)	94.8(1)
N(2)–N(1)–Pd(1)	127.8(11)	N(2)–N(1)–Pd(2)	122.9(11)
Pd(1)–N(1)–Pd(2)	109.2(7)	N(1)–N(2)–C(3)	131.6(14)
Pd(1)–P(1)–C(1)	110.6(6)	Pd(2)–P(3)–C(1)	111.1(6)
Pd(1)–P(2)–C(2)	112.2(6)	Pd(2)–P(4)–C(2)	110.0(5)

TABLE 7. Selected bond parameters for **2f**

Bond distances (Å)			
Pd(1)–Pd(1a)	3.096(1)	Pd(1)–Cl(1)	2.317(2)
Pd(1)–P(1)	2.355(2)	Pd(1)–P(2)	2.326(2)
Pd(1)–N(1)	1.984(4)	N(1)–N(2)	1.211(1)
N(2)–C(2)	1.339(11)	C(5)–F(1)	1.304(17)
Bond angles (°)			
P(1)–Pd(1)–P(2)	170.0(1)	Cl(1)–Pd(1)–N(1)	176.4(1)
P(1)–Pd(1)–Cl(1)	94.8(1)	P(1)–Pd(1)–N(1)	88.2(1)
P(2)–Pd(1)–Cl(1)	92.1(1)	P(2)–Pd(1)–N(1)	85.1(2)
N(2)–N(1)–Pd(1)	128.7(4)	Pd(1)–P(1)–C(1)	110.7(2)
Pd(1)–N(1)–Pd(1a)	102.6(1)	N(1)–N(2)–C(2)	135.3(6)

displacement of the diazenido ligand upon reaction with an excess of chloride ion.

The reactivity of the new diazenido adducts **2** was further examined by using $HBF_4 \cdot OEt_2$. No reaction was observed even in the presence of excess of the protic agent. The lack of reactivity at the outer nitrogen of the N_2R ligand could be better understood in the presence of calculations of the electron density distribution within the coordinated ligand. Finally, it is interesting to note the high stability of arenediazenido derivatives $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_2Ar)][BF_4]$ as compared to that of the nitrosyl species $[Pd_2Cl_2(\mu\text{-}NO)(dppm)_2][BF_4]$ [4]. Theoretical studies could be extremely informative on this point.

Supplementary material

Tables with the final atomic coordinates for hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles, and a listing of calculated and observed structure factors are available from the authors on request.

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