Journal of Organometallic Chemistry, 418 (1991) 119–126
Elsevier Sequoia S.A., Lausanne
JOM 22016

The reactivity of $Pd(P^tBu_3)_2$ towards the oxonium ion. Crystal structure of *trans*-$[(^tBu_3P)_2Pd(H)(CH_3CN)]BPh_4$

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(Received April 3rd, 1991)

Abstract

The reaction of $Pd(P^tBu_3)_2$ with the strong acids $H_3O^+X^-$, ($X = BF_3OH$, BF_4), gives the thermally unstable hydrides *trans*-$[(^tBu_3P)_2Pd(H)(H_2O)]X$. The thermally stable hydrides *trans*-$[(^tBu_3P)_2Pd(H)(CH_3CN)]X$ were obtained by substitution of the water molecule by CH_3CN. The reaction of the aquo-hydrides with CO, yielding $[Pd(CO)(P^tBu_3)]_2$ and the crystal structure of *trans*$[(^tBu_3P)_2Pd(H)(CH_3CN)]BPh_4$ are also reported.

Introduction

As a part of our program on the study of the reactions of O–H bonds with late-transition metal complexes we recently investigated the reactions of $Pd(PCy_3)_2$ with phenols [1,2] and H_3O^+ [3,4]. We next examined the influence on the reported reactions of structural modifications of the phosphino ligands; although PCy_3 and P^tBu_3 are comparable in terms of their basicity [5] and steric hindrance [6], quite different behaviour was observed for $Pd(PCy_3)_2$ and $Pd(P^tBu_3)_2$ in the reaction with phenol. The phenoxo-palladium(II) hydride *trans*-$[(Cy_3P)_2Pd(H)(OAr)] \cdot ArOH$ [1,2] was quantitatively obtained by oxidative addition of phenol to $Pd(PCy_3)_2$ whereas the reaction of phenol with $Pd(P^tBu_3)_2$ yielded $[Pd_2(P^tBu_2H)_2(\mu\text{-}P^tBu_2)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_5O)] \cdot 3C_6H_5OH$ [7].

We report here the reaction of $Pd(P^tBu_3)_2$ with H_3O^+ and compare the results with those for the reactions involving $Pd(PCy_3)_2$ [3,4]. The crystal structure of the

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cationic hydride *trans*-$[(^tBu_3P)_2Pd(H)(CH_3CN)]BPh_4$ has also been determined. The role played by cationic palladium hydrides in some homogeneously-catalysed processes has been recently reviewed by Zudin et al. [8].

Results and discussion

Treatment of toluene solutions of $Pd(P^tBu_3)_2$ (**1**) at −78°C with the strong acids $H_3O^+X^-$ ($X = BF_3OH, BF_4$) resulted in precipitation of white powdery solids, characterization of which was prevented by their extreme thermal instability; they could be filtered off at low temperature and sealed in ampoules under nitrogen, but they rapidly darkened and decomposed above 0°C. Any attempt to prepare solutions of the compounds failed, and rapid decomposition with the formation of a black precipitate was observed when the powders were dissolved at low temperatures in $CDCl_3$, thf-d_8, CD_3OD, or $(CD_3)_2CO$.

A reasonable suggestion for the structure of these products can be made on the basis of an analogy with the outcome of the reaction of $Pd(PCy_3)_2$ with $H_3O^+X^-$ which gave the products of oxidative addition of H_3O^+ [4] i.e. *trans*$[(Cy_3P)_2Pd(H)(H_2O)]X$ (**3a**, $X = BF_3OH$; **2b**, $X = BF_4$), as white crystalline solids. The solid state IR spectra of the aquo-hydrides **2a,b** showed signals attributable to the Pd-bound water molecule ($\nu_{as}(OH)$ 3520s, $\nu_s(OH)$ 3440s, $\delta(HOH)$ 1630s) and to the Pd–hydride moiety ($\nu(PdH)$ 2115w, $\delta(PdH)$ 720m); solution ^1H NMR spectra in acetone-d_6 showed the hydride resonance as a triplet ($^2J(PH)$ 4.3 Hz) at δ −18.3 [4].

If the analogy with the behaviour of the PCy_3 derivative is correct, the expected structure for the white powders obtained from **1** is *trans*-$[(P^tBu_3)_2Pd(H)(H_2O)]X$ (**3a**, $X = BF_3OH$; **3b**, $X = BF_4$). However, we were able to observe only the signals attributable to the metal-bound water molecule in the solid state IR spectrum ($\nu_{as}(OH)$ 3520s, $\nu_s(OH)$ 3440s, $\delta(HOH)$ 1630m), and no signals attributable to the Pd–H moiety could be detected in the IR or in the ^1H NMR spectra.

An indirect confirmation of the structure of **3a,b** came from exchange experiments with CH_3CN. The solids **3a,b** were filtered off at low temperature and rapidly dissolved in cold CH_3CN, and the pale yellow solutions were evaporated to dryness to give the thermally stable compounds *trans*-$[(P^tBu_3)_2Pd(H)(CH_3CN)]X$ (**4a,b**), which were fully characterized: signals attributable to the nitrile ligand are observable in the IR spectrum (2320vw, 2280w [$\nu(CN)$]), and the ^1H NMR spectrum (CD_3CN) (δ 1.96 [s, 3H]); other signals in the ^1H NMR spectrum arise from the *trans*-$^tBu_3P$ ligands (1.50 [t, $^3J(PH) + {}^5J(PH) = 13.0$ Hz, 54 H]) and from the Pd-bound hydride (16.3 [t, $^2J(PH) = 9.0$ Hz, 1H]).

Complexes **4a,b** can also be prepared by treatment of $Pd(P^tBu_3)_2$ with $H_3O^+X^-$ in a 1/1 CH_3CN/toluene mixture. The substitution of the metal-bound water molecule by CH_3CN was previously observed for the PCy_3 derivatives **2a,b** and *trans*-$[(Cy_3P)_2Pd(H)(CH_3CN)]X$ (**5a,b**) were isolated. Both the aquo-hydrides **2a,b** and the nitrile derivatives **5a,b** were shown to be thermally stable, though **2a,b** were much less stable than **5a,b** towards anion exchange [3,4].

In the case of P^tBu_3 derivatives prepared in this work the replacement of the water molecule by CH_3CN considerably increases the thermal stability of the Pd^{II} hydride. The greater affinity of the metal toward nitrile ligands than towards water is well documented in the case of cationic platinum hydrides [9,10].

The large difference between the thermal stability of the complexes *trans*-$[(R_3P)_2Pd(H)(H_2O)]X$ for R = ^{t}Bu and Cy is not easy to explain; at the very least identification of the thermal decomposition products of the P^tBu_3 derivative is essential to throw light on the question. A reasonable hypothesis, to be confirmed by mechanistic studies, is that the decomposition occurs through cyclometalation of one or more of the t-butyl substituents; this would be consistent with analogous decomposition mechanisms reported for Pt^{II} and Pd^{II} hydrides containing P^tBu_3 [11–15] and with our results for the reaction of $Pd({}^tBu_3)_2$ with phenol [7].

Finally, the reaction of **3a,b** with carbon monoxide gives $[Pd(CO)(P^tBu_3)]_2$ [16], as that of **2a,b** gives $[Pd(CO)(PCy_3)]_3$.

Structural characterization of *trans*-$[({}^tBu_3P)_2Pd(H)(CH_3CN)]Bph_4$ (6)

The derivative *trans*-$[({}^tBu_3P)_2Pd(H)(CH_3CN)]BPh_4$ (**6**) was made by replacing the BF_3OH^- anion of complex **4a** by $NaBPh_4$, and gave crystals suitable for an X-ray study. Crystals of **6** contain discrete *trans*-$[({}^tBu_3P)_2Pd(H)(CH_3CN)]^+$ cations and tetraphenylborate anions. An ORTEP drawing of the cation is shown in Fig. 1 together with the atom labelling. Relevant bond distances and angles are listed in Table 1. The Pd atoms has a distorted square planar coordination; the Pd atom is strictly coplanar with the P and N atoms (maximum elevation 0.004 Å) but the angles around the Pd centre show significant deviations from 90°, [P(1)–Pd–N(1) 100.6(1), P(2)–Pd–N(1) 99.2(2), P(1)–Pd(1)–P(2) 159.9(1)°], as was found for *trans*-$[(Cy_3P)_2Pd(H)(OC_6H_5)] \cdot C_6H_5OH$ and *trans*-$[(Cy_3P)_2Pd(H)(OC_6F_6)] \cdot C_6F_5OH$ [1,2].

As expected, the acetonitrile ligand coordinates to the metallic centre through the nitrogen atom. The Pd–N distance in **6** [2.122(4) Å] is comparable with that in the tetracoordinated Pd complex $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2 \cdot CH_3CN$ [2.065(14)]

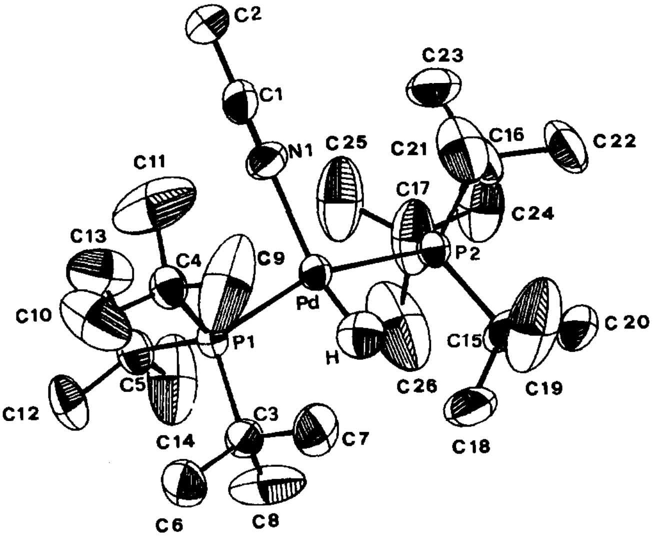

Fig. 1. ORTEP drawing of *trans*-$[({}^tBu_3P)_2Pd(H)(CH_3CN)]^+$ showing the atom labelling. For sake of clarity H(Me) atoms have been omitted.

Table 1

Selected bond distances (A) and angles (°)

Pd–P(1)	2.380(1)	P(2)–C(15)	1.908(5)
Pd–P(2)	2.377(1)	P(2)–C(16)	1.917(7)
Pd–N(1)	2.122(4)	P(2)–C(17)	1.892(7)
N(1)–C(1)	1.137(7)	C–C(^{t}Bu) mean	1.52_2
C(1)–C(2)	1.467(8)	B(1)–C(27)	1.694(6)
P(1)–C(3)	1.925(5)	B(1)–C(33)	1.685(6)
P(1)–C(4)	1.898(5)	B(1)–C(39)	1.683(6)
P(1)–C(5)	1.924(6)	B(1)–C(45)	1.677(6)
P(1)–Pd–N(1)	100.6(1)	Pd–P(2)–C(16)	108.3(2)
P(2)–Pd–N(1)	99.2(1)	Pd–P(2)–C(17)	110.5(2)
P(1)–Pd–P(2)	159.9(1)	C–C–C(^{t}Bu) mean	107_2
Pd–N(1)–C(1)	178.6(5)	C(27)–B(1)–C(33)	111.5(3)
N(1)–C(1)–C(2)	178.8(6)	C(27)–B(1)–C(39)	113.9(3)
Pd–P(1)–C(3)	112.2(2)	C(27)–B(1)–C(45)	102.3(3)
Pd–P(1)–C(4)	106.3(2)	C(33)–B(1)–C(39)	103.4(3)
Pd–P(1)–C(5)	108.2(2)	C(33)–B(1)–C(45)	113.0(3)
Pd–P(2)–C(15)	112.3(2)	C(39)–B(1)–C(45)	113.0(3)

[17]. Pd-acetonitrile complexes with other ligands exhibit the same range of distances for the Pd–N bond length (2.114(4) and 2.101(6) Å in $(CH_3CN)_2Pd(PP)PdCl_2$, PP = 2,3-bis(diphenylphosphino)N-methyl-maleimide [18]; 2.086(7) Å in $[Pd(CH_2CHCMeCH_2CH_2CH{=}CMe_2)(MeCN)]^+$ [19] and 2.10(1) Å in $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2]^+$ [20].

The CH_3CN ligand is almost exactly linear, the N(1)–C(1)–C(2) angle being 178.8(6)°.

The idealized molecular symmetry of the cation is C_s-*m*, with a mirror plane passing through the Pd atom and the nitrile ligand; the symmetry relationship between the P^tBu_3 ligands is broken only by the methyl C-atoms. The Pd–P bond lengths [2.380(1) and 2.377(1) Å] appear to be longer than those commonly observed for *trans*-metal-phosphine complexes. On the other hand, the P–C distances [average 1.91(1) Å] are only slightly longer than in $[(P^tBu_2H)_2Pd_2(\mu\text{-}P^tBu_2)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_5O)]$, (average 1.881 Å [7]).

The contacts between the C(11), C(14), C(23) and C(25) atoms, on one hand, and the N(1) atom, on the other hand, [3.537, 3.148, 3.435 and 3.365 Å, respectively] suggest the possibility of C–H ··· acceptor [21] intramolecular interactions, although evidence cannot be derived from calculated positions of the methylic hydrogen atoms.

The tetraphenylborate anion presents a rather distorted geometry around the B atom, the two opposite angles C(33)–B(1)–C(39) and C(27)–B(1)–C(45) being much narrower than the others [average 103(1) vs. 113(1)°].

Experimental

Unless otherwise stated, all procedures were carried out under prepurified nitrogen or argon by standard Schlenck techniques. $Pd(P^tBu_3)_2$ was prepared as described previously [22]. Solvents were refluxed over an appropriate drying agent (in parentheses) and distilled prior to use: toluene (Na), CH_3CN and CD_3CN (CaH_2).

IR spectra were recorded with a Perkin–Elmer 283-B spectrometer. ^{1}H-NMR spectra were recorded on a Varian XL-100 or XR-300 spectrometer; chemical shifts are reported relative to Me_4Si.

*Preparation of trans-[($^tBu_3P)_2Pd(H)(H_2O)]X$ (**3a,b**)*

A solution of $BF_3 \cdot Et_2O$ (0.315 mmol) in toluene (3 mL) containing 0.1 mL of water was added dropwise at −78°C to a solution of $Pd(P^tBu_3)_2$ (0.161 g, 0.315 mmol) in toluene (5 mL). A white solid began to separate during the addition and the suspension was stirred at −78°C for 1.5 h. The white solid (0.113 g, 58% yield) was filtered off and vacuum dried at −78°C. The BF_4^- derivative was prepared analogously by mixing at −78°C equimolar amounts of $Pd(P^tBu_3)_2$ in toluene and an aqueous solution (35%) of HBF_4. Both complexes are thermally unstable and were converted into nitrile derivatives by substitution the water molecule with CH_3CN (see below).

*Preparation of trans-[($^tBu_3P)_2Pd(H)(CH_3CN)]BF_3OH$ (**4a**)*

Method (a). *trans*-$[(^tBu_3P)_2Pd(H)(H_2O)]BF_3OH$ (0.156 g, 0.254 mmol) was dissolved in CH_3CN (10 mL) at −50°C and the solution was allowed to warm at room temperature then, after 1 h, concentrated to ca. 2 mL. Et_2O (10 mL) was added, the white solid that separated was filtered off and vacuum dried (0.085 g, 0.133 mmol, 52.5% yield). Anal. Found: C, 48.53; H, 9.09; N, 1.92. $C_{26}H_{59}BF_3NOP_2Pd$ calc.: C, 48.90; H, 9.20; N, 2.19%. IR (Nujol, cm^{-1}) 3220s [ν(OH)], 2320vw, 2280w [ν(CN)], 1050vs [ν(BF)]. ^{1}H NMR (CD_3CN) δ 1.96 [s, 3H, CH_3CN], 1.50 [t, $^3J(PH) + {}^5J(PH) = 13.0$ Hz, 54H, P^tBu_3), −16.3 [t, $^2J(PH) = 9.0$ Hz, 1H, Pd-*H*].

Method (b). To a solution of $Pd(B^tBu_3)_2$ (0.756 g, 1.48 mmol) in 30 mL of a 1/1 toluene/CH_3CN mixture were added 0.1 mL of water and 0.19 mL of $BF_3 \cdot Et_2O$. The solution was kept at room temperature for 1.5 h then concentrated to ca. 10 mL and Et_2O (20 mL) was added. The microcrystalline solid was filtered off and vacuum dried (0.644 g, 1.01 mmol, 68% yield). Analytical and spectroscopic data were identical to those of the complex prepared by method (a).

*Preparation of trans-[($^tBu_3P)_2Pd(H)(CH_3CN)]BF_4$ (**4b**)*

Complex **4b** was prepared by methods (a) (by dissolving **3b** in CH_3CN) and (b) (by treating $Pd(P^tBu_3)_2$ with HBF_4 in CH_3CN/toluene) above. Anal. Found: C, 49.2; H, 8.95; N, 1.92. $C_{26}H_{59}BF_4NP_2Pd$ calc.: C, 48.8; H, 9.14; N, 2.18%. IR (Nujol, cm^{-1}) 2320vw, 2280w [ν(CN)], 1050vs [ν(BF)]. ^{1}H NMR (CD_3CN) δ 1.96 [s, 3H, CH_3CN], 1.50 [t, $^3J(PH) + {}^5J(PH) = 13.0$ Hz, 54H, P^tBu_3), −16.3 [t, $^2J(PH) = 9.0$ Hz, 1H, Pd-*H*].

*Preparation of trans-[($^tBu_3P)_2Pd(H)(CH_3CN)]BPh_4$ (**6**)*

A solution of *trans*-$[(^tBu_3P)_2Pd(H)(CH_3CN)]BF_3OH$ (0.222 g, 0.348 mmol) in CH_3CN (20 mL) was added dropwise to a solution of $NaBPh_4$ (0.120 g, 0.350 mmol) in CH_3CN (10 mL). After 3 h at room temperature the grey powder was filtered off, the filtrate concentrated to ca. 20 mL, and Et_2O slowly added. Crystals suitable for X-ray analysis were formed and were filtered off and vacuum dried (0.134 g, 0.164 mmol, 47% yield). Anal. Found: C, 69.96; H, 9.66; N, 1.46. $C_{50}H_{78}BNP_2Pd$ calc.: C, 68.8; H, 8.94; N, 1.60%. IR (Nujol, cm^{-1}) 3050m [ν(CH)], 2300vw, 2280w [ν(CN)], 1580m [ν(CC)]. ^{1}H NMR (CD_3CN) δ 7.35–6.80 (m, 20H, C_6H_5), 1.96 (s, 3H, CH_3CN), 1.50 (t, ^3J(PH) + ^5J(PH) = 13.0 Hz, 54H, P^t*Bu*$_3$), − 16.30 (t, ^2J(PH) = 9.0 Hz, 1H, Pd-*H*).

*Reaction of **3a** with CO*

Complex **3a** (0.467 g, 0.733 mmol) was dissolved in CH_3CN (30 mL) under a CO atmosphere. The colourless solution slowly turned orange, and a yellow crystalline solid began to separate. After 2 h at room temperature the solid was filtered off and vacuum dried (0.401 g). It was identified as [Pd(CO)(P^{t}Bu$_3$)]$_3$ from its analytical and spectroscopic data [16]. The same reaction took place when complex **3b** was used in place of **3a**. Anal. Found: C, 45.90; H, 8.04. $C_{39}H_{81}O_3P_3Pd_3$ calc.: C, 46.30; H, 8.07%. IR (Nujol, cm^{-1}) 1843s, 1802s, 1795s [ν(CO)]. ^{1}H NMR (C_6D_6) δ 1.52 (d, ^3J(PH) = 10 Hz).

Data collection and structure determination

Crystal data and details of the data collection for **6** are reported in Table 2. Diffraction data were collected at room temperature with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). The unit cell was determined from a least-squares fit of 25 reflections. Data were corrected for Lorentz-polarization effects. Empirical absorption correction was

Table 2

Crystal data and details of measurements for *trans*-[Pd(P^{t}Bu$_3$)$_2$(H)(CH_3CN)]·B(C_6H_5)$_4$

Formula	$C_{50}H_{78}BNP_2Pd$
M_r	833.9
Crystal size (mm)	0.25 × 0.30 × 0.35
System	monoclinic
Space group	$P2_1/c$
a (Å)	13.289(4)
b (Å)	16.418(5)
c (Å)	22.764(5)
β (°)	90.89(2)
U (Å^3)	4966.02
Z	4
F(000)	1864
D_{calc} (g cm^{-3})	1.12
λ(Mo-K_α) (Å)	0.71069
μ(Mo-K_α) (cm^{-1})	4.11
θ range (°)	2.5–25
ω-scan width (°)	0.7 + 0.35 tan θ
Requested counting $\sigma(I)/I$	0.01
Prescan rate (deg min^{-1})	8
Prescan acceptance $\sigma(I)/I$	0.5
Maximum scan time (s)	100
Range of reflections measured ($h_{min}h_{max}, k_{min}k_{max}, l_{min}l_{max}$)	− 15 15,0 19,0 27
Measured reflections	9264
Unique observed reflections [$I_o > 2.5\sigma(I_o)$]	5253
No. of refined parameters	331
R, R_w [a], g [a]	0.040, 0.044, 0.000746

[a] $R_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma F_o w^{1/2})$, where $w = k/[\sigma(F) + |g|F^2]$.

Table 3

Fractional atomic coordinates

Atom	*x*	*y*	*z*
Pd	0.23223(2)	0.66309(2)	0.20412(1)
P(1)	0.31793(8)	0.57989(6)	0.13543(5)
P(2)	0.11520(8)	0.75819(7)	0.24221(5)
N(1)	0.2923(4)	0.6169(3)	0.2844(2)
C(1)	0.3265(4)	0.5923(3)	0.3269(2)
C(2)	0.3715(5)	0.5622(4)	0.3820(2)
C(3)	0.3040(3)	0.6202(3)	0.0563(2)
C(4)	0.2565(4)	0.4757(3)	0.1389(2)
C(5)	0.4596(3)	0.5691(3)	0.1524(2)
C(6)	0.3615(6)	0.5750(4)	0.0096(2)
C(7)	0.1944(5)	0.6165(7)	0.0380(3)
C(8)	0.3372(6)	0.7098(3)	0.0556(3)
C(9)	0.1446(5)	0.4854(4)	0.1358(5)
C(10)	0.2871(5)	0.4148(3)	0.0931(3)
C(11)	0.2834(8)	0.4367(5)	0.1993(3)
C(12)	0.5073(6)	0.6498(5)	0.1451(7)
C(13)	0.5149(5)	0.5072(7)	0.1171(4)
C(14)	0.4801(5)	0.5532(7)	0.2154(4)
C(15)	0.0645(5)	0.8307(4)	0.1833(2)
C(16)	0.0022(5)	0.6990(4)	0.2714(4)
C(17)	0.1748(5)	0.8191(4)	0.3041(3)
C(18)	0.1554(8)	0.8890(6)	0.1687(5)
C(19)	0.0466(8)	0.7925(6)	0.1253(3)
C(20)	−0.0266(5)	0.8832(4)	0.2011(3)
C(21)	−0.0627(7)	0.6694(6)	0.2161(5)
C(22)	−0.0680(5)	0.7509(5)	0.3107(4)
C(23)	0.0359(6)	0.6232(5)	0.3006(4)
C(24)	0.1228(5)	0.8998(4)	0.3205(3)
C(25)	0.1769(8)	0.7640(6)	0.3611(3)
C(26)	0.2849(5)	0.8342(5)	0.2895(4)
B(1)	0.2951(3)	0.1626(3)	0.9896(2)
C(27)	0.3692(2)	0.1541(2)	0.9301(1)
C(28)	0.3276(2)	0.1700(2)	0.8746(1)
C(29)	0.3847(2)	0.1579(2)	0.8245(1)
C(30)	0.4835(2)	0.1298(2)	0.8298(1)
C(31)	0.5252(2)	0.1139(2)	0.8852(1)
C(32)	0.4680(2)	0.1261(2)	0.9354(1)
C(33)	0.2136(2)	0.2407(2)	0.9825(1)
C(34)	0.1231(2)	0.2385(2)	1.0126(1)
C(35)	0.0575(2)	0.3048(2)	1.0098(1)
C(36)	0.0823(2)	0.3732(2)	0.9767(1)
C(37)	0.1729(2)	0.3754(2)	0.9465(1)
C(38)	0.2385(2)	0.3092(2)	0.9494(1)
C(39)	0.3585(2)	0.1845(2)	1.0522(1)
C(40)	0.3214(2)	0.1583(2)	1.1060(1)
C(41)	0.3689(2)	0.1824(2)	1.1583(1)
C(42)	0.4535(2)	0.2326(2)	1.1567(1)
C(43)	0.4905(2)	0.2588(2)	1.1029(1)
C(44)	0.4431(2)	0.2347(2)	1.0507(1)
C(45)	0.2382(2)	0.0715(2)	0.9913(1)
C(46)	0.2858(2)	0.0067(2)	1.0199(1)
C(47)	0.2435(2)	−0.0710(2)	1.0174(1)
C(48)	0.1537(2)	−0.0839(2)	0.9863(1)
C(49)	0.1061(2)	−0.0191(2)	0.9576(1)
C(50)	0.1484(2)	0.0586(2)	0.9601(1)

made by the Walker and Stuart method [23]. All calculations were performed with the SHELX76 and SHELX86 systems of programs [24]. The structure was solved by direct methods; subsequent difference Fourier syntheses combined with least-squares refinement allowed the location of all non-hydrogen atoms. The structure was refined by full-matrix least-squares calculations; the weighting factor used was $w = k/\sigma^2(F) + |g|F^2$, where $g = 0.000746$.

The hydride H-atom was directly located in a difference Fourier map and not refined, except for its isotropic thermal parameter. The remaining hydrogen atoms were placed in calculated positions [d(C–H) 1.08 Å], and refined "riding" on their respective carbon atoms. Phenyl groups were treated as "rigid hexagons".

The final refinement of all positional and thermal parameters involved anisotropic treatment of thermal vibrations for all non-H atoms of both the cation and the anion. The final difference Fourier map showed a residual peak of 0.6 e Å^{-3} near the Pd atom. Fractional atomic coordinates are reported in Table 3. A complete list of bond distances and angles, and lists of thermal parameters and observed and calculated structure factors are available from the authors.

Acknowledgements

We thank the "Ministero dell'Università e della Ricerca Scientifica e Tecnologica" and CNR (Rome) for financial support.

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