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# Reactions of $[MCl_2(ppqMe_2)_2]$ (M=Pd, Pt) with $I^-$ and with $CF_3SO_3H/I^-$ including the synthesis and X-ray crystal structure of the palladium phosphidoxo complex $[Pd_2(\mu\text{-}I)_2\{(PPh_2O)_2H\}_2]$

**Stephen B. Colbran*, Don C. Craig** and **Seri Bima Sembiring**

*Department of Inorganic and Nuclear Chemistry, University of New South Wales, P.O. Box 1, Kensington, NSW 2033 (Australia)*

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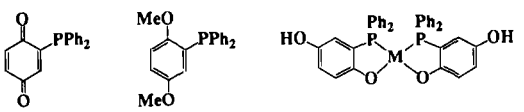
**Abstract**

The compounds $[MI_2(ppqMe_2)_2]$ (**5**: M=Pd; **6**: M=Pt) have been synthesised and their thermolyses and reactions with strong acids investigated. Thermolysis of **5** in the presence of excess iodide ion caused complete decomposition of the complex whereas the corresponding reaction of **6** gave the P~O chelated complex $[Pt(ppqMe)_2]$ (**7**) in good yield. Treatment of **5** with $CF_3SO_3H/I^-$ facilitated the loss of the 2,5-dimethoxyphenyl substituent from each phosphine ligand and gave the iodo-bridged palladium(II) phosphidoxo complex $[Pd_2(\mu\text{-}I)_2\{(PPh_2O)_2H\}_2]$ (**8**). An X-ray single crystal structural analysis of **8** is reported.

## Introduction

We have initiated a general investigation of transition metal complexes with redox-active ligands having paraquinonyl-, parasemiquinonyl- or parahydroquinonyl substituents. Free phosphines with parabenzoquinonyl substituents, for example the diphenylphosphino- substituted quinone ppq, cannot be isolated because of the facile addition of phosphines to parabenzoquinones; i.e. parabenzoquinones and phosphines are mutually incompatible moieties [1, 2]. One synthetic approach that overcomes the incompatibility of the centres in ppq is to 'protect' the quinone as its bis-methylether until complexes are formed. After coordination the reactive phosphorus lone pair is 'tied-up' and the quinonyl moiety can be released to give the targeted quinonylphosphine complexes. We have reported this approach to platinum and palladium complexes of ppq using 1,4-dimethoxy-2-diphenylphosphino-benzene, $ppqMe_2$, as the 'protected' precursor ligand [1]. The complexes *trans*-$[MCl_2(ppqMe_2)_2]$ (**1**: M=Pd; **2**: M=Pt) were prepared and the methoxy groups cleaved using $BBr_3$ to give after workup the chelated hydroquinonyl complexes *cis*-$[M(ppqH)_2]$ (**3**: M=Pd; **4**: M=Pt) [1].




ppq ppqMe$_2$ [M(ppqH)$_2$]

**3** M=Pd; **4** M=Pt

There are several reports of methyliodide elimination from platinum complexes with both iodo and *ortho*-anisole-substituted phosphine ligands to give chelated phenoxyphosphine complexes [3]. Also, strong acids (for example, concentrated HBr and HI) are well known to cleave arylmethyl ethers such as the methoxy groups in $ppqMe_2$ and its complexes [4]. Therefore, in our initial attempts to cleave the methoxy groups in **1** and **2**, we first prepared their iodo derivatives $[MI_2(ppqMe_2)_2]$ (**5**: M=Pd; **6**: M=Pt) and then investigated the reactions of **5** and **6** with strong acid ($CF_3SO_3H$) and with heating. This paper describes our findings from these studies.

## Experimental

All reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk and cannula techniques. Solvents were dried by the usual methods and were distilled immediately prior to use from the appropriate drying agent under an atmosphere of dinitrogen. The complexes $[MCl_2(ppqMe_2)_2]$ (M=Pd,

*Author to whom correspondence should be addressed.

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Pt) were prepared as detailed elsewhere [1]. Other chemicals were procured from commercial sources and were used as obtained.

$^1$H NMR spectra were recorded on Varian EM360 (60 MHz) or Bruker AM500 (500 MHz) NMR spectrometers. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CXP300 spectrometer (operating at 121.46 MHz) and are referenced relative to external 0.5% $KH_2PO_4$ in $D_2O$ (high frequency positive) which was also used for the lock. Infrared spectra were recorded on Perkin-Elmer 500B or Hitachi 260-10 infrared spectrometers. Elemental analyses were determined by the University of NSW microanalytical service.

*Preparation of trans-[$PdI_2(ppqMe_2)_2$]*

A mixture of [$PdCl_2(ppqMe_2)_2$] (0.1 g, 0.12 mmol) and KI (0.50 g, 3 mmol) was stirred in dry distilled acetone (25 ml) for 2 h. The colour of the solution changed from yellow to red–brown immediately after the addition of KI. The solvent was removed under vacuum and the resulting solid residue extracted with $CH_2Cl_2$. Red–brown crystals of the product (0.085 g, 71%) were obtained by adding ether to the extract solution. $^1$H NMR ($CDCl_3$): $\delta$ 7.79–7.76 (m, 8H, *Ph*). 7.36–7.31 (m, 12H, *Ph*), 6.88 (dd: 8.9, 3.0 Hz, 2H, $C_6H_3$), 6,79 (dd: 5.3, 2.9 Hz, 2H, $C_6H_3$), 6.77 (dd: 5.5, 3.0 Hz, 2H, $C_6H_3$), 3.81 (s, 6H, O*Me*), 3.80 (s, 6H, O*Me*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 5.66 (s) ppm. IR (KBr disk; $cm^{-1}$): 3077m, 3057m, 3004m, 2956m, 1607m, 1587m, 1490vs, 1467s, 1439vs, 1409m, 1277vs, 1228vs, 1185m, 1144w, 1098m, 1071w, 1046s, 1023s, 878w, 812m, 750s, 697vs, 573m, 545w, 510vs, 434w. *Anal.* Found: C, 47.72; H, 3.77. Calc. for ($C_{40}H_{38}O_4I_2P_2Pd$): C, 47.80; H, 3.77%.

*Preparation of cis/trans-[$PtI_2(ppqMe_2)_2$]*

Stirring [$PtCl_2(ppqMe_2)_2$] (0.1 g, 0.11 mmol) and KI (0.50 g, 3 mmol) in dry distilled acetone (25 ml) for 20 h gave, after workup, the product (100 mg, 87%) as a mixture of *cis* and *trans* isomers. $^1$H NMR ($CDCl_3$): $\delta$ 7.81–7.77 (m, 8H, *Ph*), 7.35–7.24 (m, 12H, *Ph*), 6.96 (td: 11.1, 3.0 Hz, 2H, $C_6H_3$, *trans* isomer), 6.88 (dd: 8.9, 3.1 Hz, 2H, $C_6H_3$, *trans* isomer), 6.77 (dt: 8.9, 2.7 Hz, 2H, $C_6H_3$, *trans* isomer), 6.63 (m, broad, 2H, $C_6H_3$, *cis* isomer), 6.36 (m, broad, 4H, $C_6H_3$, *cis* isomer), 3.64 (s, 6H, O*Me*, *trans* isomer), 3.57 (s, 6H, O*Me*, *trans* isomer), 3.52 (s, O*Me*, *cis* isomer), 3.23 (s, broad, O*Me*, *cis* isomer) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 6.82 (s, $^{195}$Pt satellites: d, $^1J$ ($^{31}P$–$^{195}Pt$) 2570 Hz, *trans* isomer), $\delta$ 5.74 (s, $^{195}$Pt satellites: d, $^1J$ ($^{31}P$–$^{195}Pt$) 3651 Hz, *cis* isomer) ppm. IR (paraffin mull; $cm^{-1}$): 2731w, 2674w, 1606w, 1584w, 1492vs, 1441vs, 1398m, 1297w, 1275m, 1233vs, 1185m, 1141m, 1099m, 1071w, 1042vs, 1020m, 873w, 817m, 749m, 739m, 724m, 699s, 691s, 603m, 520vs, 503s, 471w, 439w, 400w. *Anal.* Found: C, 43.82; H, 3.37. Calc. for ($C_{40}H_{38}O_4I_2P_2Pt$): C, 43.92; H, 3.48%.

*Thermolysis of cis-[$PdI_2(ppqMe_2)_2$]*

Heating *cis*-[$PdI_2(ppqMe_2)_2$] (60 mg) and KI (0.25 g) in 2-methoxyethanol at reflux caused rapid decomposition of the complex. Only Pd metal and some intractable solids were isolated from this reaction.

*Preparation of cis-[$Pt(ppqMe)_2$]*

A solution of [$PtCl_2(ppqMe_2)_2$] (0.10 g, 0.11 mmol) and KI (0.5 g, 3 mmol) in 2-methoxyethanol was heated at reflux for 18 h. Removal of the solvent and recrystallisation from $CH_2Cl_2$/MeOH gave the product as an off-white powder (50 mg, 56%). $^1$H NMR ($CDCl_3$): $\delta$ 7.31–7.26 (m, 12H, *Ph*), 7.08–7.05 (m, 8H, *Ph*), 7.02 (dd: 9.2, 5.4 Hz, 2H, $C_6H_3$), 6.88 (dd: 9.2, 2.9 Hz, 2H, $C_6H_3$), 6.30 (dd: 11.4, 3.0 Hz, 2H, $C_6H_3$), 3.57 (s, 6H, O*Me*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 18.72 (s) ppm. IR (KBr disk; $cm^{-1}$): 3060w, 2937w, 2836w, 1554w, 1479vs, 1441vs, 1409s, 1267vs, 1215vs, 1184m, 1128w, 1106s, 1058m, 1037m, 1002w, 892w, 823m, 798m, 786s, 747m, 729m, 712s, 695vs, 620w, 557m, 534m, 508vs, 496s, 464w, 430w. *Anal.* Found: C, 53.11; H, 3.76. Calc. for ($C_{38}H_{32}O_4I_2P_2Pd$): C, 52.35; H, 3.80%.

*Preparation of [$Pd_2(\mu\text{-}I)_2\{(PPh_2O)_2H\}_2$]*

To a stirred solution of [$PdI_2(ppqMe_2)_2$] (100 mg, 0.1 mmol) in $CH_2Cl_2$ at room temperature was added $Et_4NI$ (300 mg, 1.17 mmol) followed by $CF_3SO_3H$ (0.2 ml). The colour turned from yellow–orange to an intense brown. The reaction mixture was heated at reflux for 30 min, cooled and stirred for 18 h. Distilled water was then added. The $CH_2Cl_2$ phase was collected, dried with anhydrous $MgSO_4$, filtered and evaporated under vacuum to give a dark red–brown powder. Deep-red crystals of the product (20–75 mg, ~20–86%) were obtained by recrystallisation from $CH_2Cl_2$–ether mixtures. $^1$H NMR ($CDCl_3$): $\delta$ 7.82–7.21 (m, 20H, *Ph*) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 80.60 (s) ppm. IR (paraffin mull, $cm^{-1}$): 2729w, 2681w, 1590w, 1577w, 1381vs, 1310m, 1265m, 1229m, 1185m, 1163w, 1110vs, 1101s, 1034vs, 1021vs, 1001m, 806m, 772m, 752s, 720vs, 694vs, 589w, 545w, 514s, 495s, 454w, 398w, 329w.

*Reaction of cis/trans-[$PtI_2(ppqMe_2)_2$] with $CF_3SO_3H/I^-$*

[$PtI_2(ppqMe_2)_2$] (70 mg, 0.06 mmol) was treated with $CF_3SO_3H/Et_4NI$ in an exactly analogous fashion to the palladium analogue, [$PdI_2(ppqMe_2)_2$] (described immediately above). $^1$H and $^{31}P\{^1H\}$ NMR

spectra of the powder (65 mg) obtained from the reaction showed it to contain several products. These were not separated or characterised.

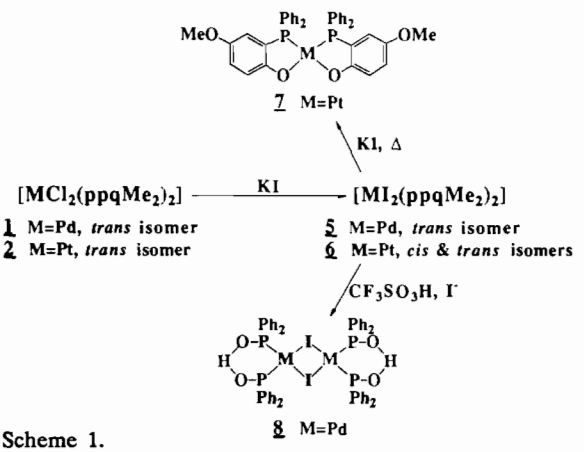
*X-ray crystallography*

*Crystal data*

$[Pd(C_{24}H_{21}P_2O_2)_2I]_2$, $M$ 1273.4, monoclinic, space group $P2_1/c$, $a = 8.512(4)$, $b = 19.788(3)$, $c = 14.841(6)$ Å, $\beta = 105.45(2)°$, $V = 2409(1)$ Å$^3$, $D_c = 1.75$ g cm$^{-3}$, $Z = 2$, $\mu$(Mo) = 21.76 cm$^{-1}$. Crystal size $0.12 \times 0.18 \times 0.14$ mm, $2\theta_{max}$ 50°, max. and min. transmission factors 0.66 and 0.80. The number of reflections was 3341 considered observed out of 4223 unique data, with $R_{merge}$ 0.011 for 147 pairs of equivalent $hk0$ reflections. Final residuals $R$ and $R_w$ were 0.027 and 0.039.

*Structure determination*

Refection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatised molybdenum radiation (λ 0.7107 Å). Data were corrected for absorption. Reflections with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. Phenyl hydrogen atoms were included in calculated positions, the remainder located in a difference Fourier, and were assigned thermal parameters equal to those of the atom to which bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full matrix least-squares. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [5]. Structure solution was by MULTAN80 [6] and refinement used BLOCKLS, a local version of ORFLS [7]. ORTEP-II [8] running on a Macintosh IIcx was used for the structural diagram, and an IBM 3090 computer was used for calculations.




Scheme 1.

## Results and discussion

Simple metathesis reactions of **1** and **2** with KI in acetone gave near quantitative yields of the corresponding iodo compounds, **5** and **6**, after ~16 h (Scheme 1). These were isolated as stable orange and red–orange crystalline solids, respectively. The $^1$H NMR spectrum of **5** showed multiplets for the phenyl substituents, three distinct multiplets for each proton of the 2,5-dimethoxyphenyl rings, and a singlet for each of the two inequivalent methoxy groups (the full data for all new complexes are listed in 'Experimental'). In the $^{31}P\{^1H\}$ NMR spectrum of **5** a singlet was observed at $\delta$ 5.70 ppm. This data clearly indicates that only a single isomer of **5** was present in solution. Analogous $[Pd(PR_3)_2X_2]$ (X = halogen or pseudohalogen) complexes usually exist as an equilibrium mixture of *cis* and *trans* isomers in solution [9, 10]. The *trans* isomer is predominant in solutions of complexes with bulkier phosphine ligands and is more likely as the halogen ligands are exchanged Cl → Br → I (e.g. $[Pd(PPh_2Me)_2Cl_2]$ gives solutions containing both *cis* and *trans* isomers whereas $[Pd(PPh_2Me)_2I_2]$ dissolves as the *trans* isomer only [10]). That the geometry of **5** is *trans* follows from consideration of these precedents and the following points: (i) $ppqMe_2$ is a relatively large phosphine, (ii) **5** is an iodo complex, (iii) **1**, the chloro analogue of **5**, is *trans* both in the solid and in solution [1]. In contrast to **5**, the platinum analogue **6** was isolated as a mixture of *cis* and *trans* isomers. This is most clearly revealed by the $^{31}P\{^1H\}$ NMR

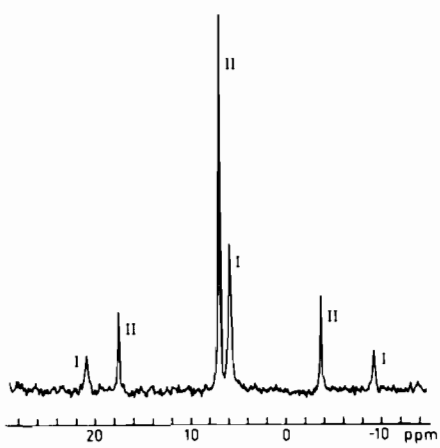



Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of a mixture of *cis*- and *trans*-$[PtI_2(ppqMe_2)_2]$ (**6**) in deuterochloroform. Peak labelling: I = *cis* isomer, II = *trans* isomer.

spectrum of **6** (Fig. 1). Two singlets with satellite doublets arising from the $^{195}Pt$ isotopomers ($^{195}Pt$: $I = 1/2$, 33.8% natural abundance) are observed. The lower field peak ($\delta$ 6.82 ppm; $^1J$ ($^{31}P$–$^{195}Pt$) 2570 Hz) can be attributed to the *trans* isomer and the higher field peak to the *cis* isomer ($\delta$ 5.74 ppm; $^1J$ ($^{31}P$–$^{195}Pt$) 3651 Hz) on the basis of the magnitudes of the $^1J$ ($^{31}P$–$^{195}Pt$) coupling constants which are unambiguous for *cis* or *trans* phosphine coordination ($^1J$ ($^{31}P$–$^{195}Pt$) for *cis* complexes is typically greater than 3500 Hz whereas $^1J$ ($^{31}P$–$^{195}Pt$) in *trans* complexes is usually less than 2800 Hz [11]). From the intensities of the peaks it may be deduced that the ratio *cis*:*trans* is ~1:3. Peaks attributable to both *cis* and *trans* isomers are also observed in the $^1H$ NMR spectrum of **6**. These were assigned by assuming that the relative abundances of *cis* and *trans* isomers were constant and thus that the corresponding peak intensities were the same in both the $^{31}P\{^1H\}$ and $^1H$ NMR spectra.

Thermolyses of **5** and **6** were investigated by heating these complexes in 2-methoxyethanol, a solvent in which methyliodide elimination had been observed on heating platinum complexes containing *ortho*-anisole substituted phosphines and iodo ligands (eqn. (1)) [3, 12].

$$[PtI_2\{P(o\text{-}MeOC_6H_4)Ph_2\}_2] \longrightarrow [Pt\{P(o\text{-}OC_6H_4)Ph_2\}_2] + 2MeI \quad (1)$$

On heating **5** only the slow thermal degradation to palladium metal and other intractable solids was observed. In contrast, **6** cleanly eliminated MeI in refluxing 2-methoxyethanol to give good yields of *cis*-[Pt(ppqMe)$_2$] (**7**) which contains two P~O chelated ppqMe ligands (Scheme 1). Again, the NMR data found for **7** are diagnostic of its structure. Thus, the $^1H$ NMR spectrum reveals multiplets for the protons of the phenyl groups and for the three inequivalent protons of each substituted phenyl ring (at $\delta$ 7.02, 6.88, 6.30 ppm), and a singlet for the remaining methoxy groups (at $\delta$ 3.57 ppm). A singlet and associated satellite doublet (from the $^{195}Pt$ isotopomer) was observed at $\delta$ 18.72 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The magnitude of the $^1J$ ($^{31}P$–$^{195}Pt$) coupling constant (3515 Hz) is conclusive for *cis* coordination of the ligands in **7** [11].

In an attempt to cleave both methoxy groups of each phosphine ligand in **5** and **6**, reactions with

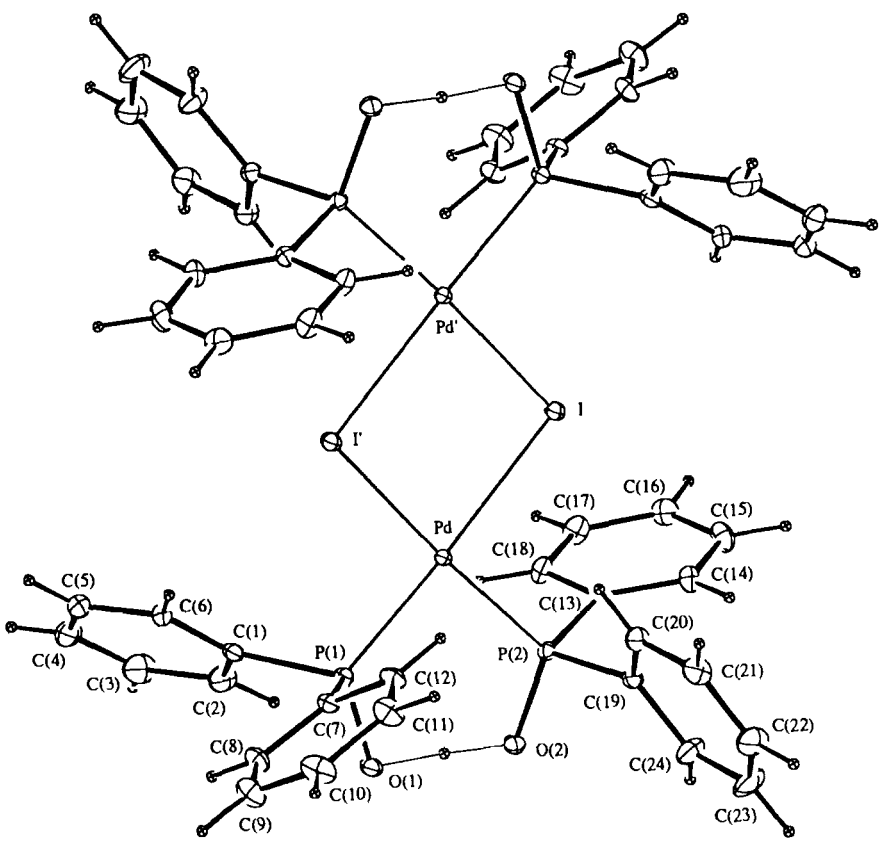



Fig. 2. Molecular structure and labelling scheme for [Pd$_2$($\mu$-I)$_2$\{(PPh$_2$O)$_2$H\}$_2$] (**8**). A crystallographic inversion centre is located at the centre of the Pd$_2$I$_2$ rhombus.

TABLE 1. Non-hydrogen atomic parameters for **8** with e.s.d.s. in parentheses

| | *x* | *y* | *z* | $B_{eq}$[a] |
|---|---|---|---|---|
| I | 0.39527(4) | 0.58084(1) | 0.46269(2) | 3.54(1) |
| Pd | 0.35222(4) | 0.45397(2) | 0.39169(2) | 2.21(1) |
| P(1) | 0.3210(1) | 0.3460(1) | 0.3376(1) | 2.58(3) |
| P(2) | 0.1583(1) | 0.4906(1) | 0.2643(1) | 2.58(3) |
| O(1) | 0.1768(4) | 0.3323(2) | 0.2503(2) | 3.42(9) |
| O(2) | 0.0423(4) | 0.4371(2) | 0.2056(2) | 3.50(9) |
| C(1) | 0.2829(6) | 0.2860(2) | 0.4220(3) | 3.46(13) |
| C(2) | 0.1204(8) | 0.2745(3) | 0.4178(4) | 5.46(20) |
| C(3) | 0.0780(11) | 0.2265(4) | 0.4753(6) | 7.92(30) |
| C(4) | 0.1973(13) | 0.1913(4) | 0.5365(5) | 7.40(30) |
| C(5) | 0.3550(10) | 0.2034(3) | 0.5425(4) | 5.87(23) |
| C(6) | 0.3994(7) | 0.2513(3) | 0.4855(4) | 4.36(16) |
| C(7) | 0.5018(6) | 0.3193(2) | 0.3054(3) | 3.10(12) |
| C(8) | 0.5248(6) | 0.2512(3) | 0.2886(4) | 4.06(15) |
| C(9) | 0.6469(7) | 0.2307(3) | 0.2508(5) | 5.54(20) |
| C(10) | 0.7489(7) | 0.2790(3) | 0.2273(5) | 5.94(22) |
| C(11) | 0.7298(7) | 0.3463(3) | 0.2443(5) | 5.57(21) |
| C(12) | 0.6058(6) | 0.3664(3) | 0.2841(4) | 3.87(15) |
| C(13) | 0.0241(5) | 0.5497(2) | 0.2996(3) | 2.85(12) |
| C(14) | −0.0010(6) | 0.6153(3) | 0.2677(4) | 3.73(14) |
| C(15) | −0.1081(7) | 0.6565(3) | 0.2985(5) | 5.13(19) |
| C(16) | −0.1903(7) | 0.6324(3) | 0.3598(4) | 4.96(18) |
| C(17) | −0.1687(7) | 0.5671(3) | 0.3896(4) | 5.06(19) |
| C(18) | −0.0614(6) | 0.5257(3) | 0.3615(4) | 4.13(15) |
| C(19) | 0.2546(6) | 0.5318(2) | 0.1840(3) | 3.18(13) |
| C(20) | 0.4183(7) | 0.5446(3) | 0.2038(4) | 4.06(15) |
| C(21) | 0.4893(8) | 0.5683(3) | 0.1358(5) | 5.47(21) |
| C(22) | 0.3955(10) | 0.5791(4) | 0.0485(5) | 7.07(28) |
| C(23) | 0.2318(11) | 0.5668(4) | 0.0263(5) | 7.73(28) |
| C(24) | 0.1604(7) | 0.5438(4) | 0.0930(4) | 5.65(21) |

[a] $B_{eq}$ (Å$^2$) is the isotropic equivalent of the anisotropic temperature factor.

TABLE 2. Interatomic distances (Å) for **8** with e.s.d.s. in parentheses[a]

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| Pd–I | 2.709(1) | Pd–I′ | 2.700(1) |
| Pd–P(1) | 2.273(1) | Pd–P(2) | 2.272(1) |
| P(1)–O(1) | 1.553(3) | P(2)–O(2) | 1.549(3) |
| P(1)–C(1) | 1.816(5) | P(2)–C(13) | 1.807(4) |
| P(1)–C(7) | 1.808(5) | P(2)–C(19) | 1.811(5) |
| C(1)–C(2) | 1.387(8) | C(13)–C(14) | 1.379(7) |
| C(2)–C(3) | 1.386(9) | C(14)–C(15) | 1.388(7) |
| C(3)–C(4) | 1.360(12) | C(15)–C(16) | 1.373(8) |
| C(4)–C(5) | 1.343(11) | C(16)–C(17) | 1.362(9) |
| C(5)–C(6) | 1.388(8) | C(17)–C(18) | 1.372(8) |
| C(6)–C(1) | 1.359(7) | C(18)–C(13) | 1.399(6) |
| C(7)–C(8) | 1.394(7) | C(19)–C(20) | 1.369(7) |
| C(8)–C(9) | 1.368(7) | C(20)–C(21) | 1.388(8) |
| C(9)–C(10) | 1.396(9) | C(21)–C(22) | 1.346(10) |
| C(10)–C(11) | 1.374(9) | C(22)–C(23) | 1.365(11) |
| C(11)–C(12) | 1.397(7) | C(23)–C(24) | 1.371(9) |
| C(12)–C(7) | 1.377(7) | C(24)–C(19) | 1.394(7) |

[a] Primes refer to the symmetry transformation $1-x$, $1-y$, $1-z$.

excess $CF_3SO_3H$ and $Et_4NI$ in dicloromethane were carried out. The reasoning that lead to this combination of reagents was based on the facts: (*i*) HI or other strong acids can effect ether cleavages as can iodide ion, and (ii) the combination of $I^-$ and $CF_3SO_3H$ should lead to an equilibrium concentration of anhydrous HI in solution. Surprisingly, the phosphidoxo complex $[Pd_2(\mu\text{-}I)_2\{(PPh_2O)_2H\}_2]$ (**8**) was isolated in variable yield (~20–86%; the latter is the best yield obtained; no attempt was made to optimise the reaction conditions) from the reaction of **5** with these reagents (Scheme 1). The reaction parallels that reported by Carty and coworkers who observed that hydrolysis of *cis*-$[PdCl_2(Ph_2PC{\equiv}CCF_3)_2]$ in refluxing aqueous ethanol–dichloromethane mixture gave $[Pd_2(\mu\text{-}Cl)_2\{(PPh_2O)_2H\}_2]$ as a major product [13]. More recently, Pringle and coworkers have demonstrated that base-promoted cleavage of a P–C bond under mild conditions can also give phosphidoxo complexes [14]. Attempted cleavage of **6** with $CF_3SO_3H/I^-$ was not as clean and always yielded many products. These have not, as yet, been characterised. Complex **8** was identified by comparison of its spectroscopic data with that of the known chloro and bromo analogues [13, 15]. Only phenyl multiplets are observed in the $^1H$ NMR spectrum of **8**. The absence of the three multiplets that are characteristic of the methoxy- and hydroxy-substituted phenyl rings in **1–7** provides clear evidence for the loss of these groups in **8**. Failure to find a $^1H$ NMR resonance for the hydroxylic protons is likely due to exchange broadening and has been noted before in other phosphidoxo systems of palladium and platinum [13–16]. The formulation of **8** is substantiated by the downfield shift observed in the $^{31}P\{^1H\}$ NMR spectrum. A singlet was observed at $\delta$ 80.60 ppm. Similar downfield shifts were reported for the chloro analogues $[M_2(\mu\text{-}Cl)_2\{(PPh_2O)_2H\}_2]$ M=Pd, Pt) [13, 15].

Compound **8** was further characterised by X-ray crystallography. Dark red crystals of **8** were obtained from dichloromethane–ether. The X-ray analysis revealed **8** crystallised in the space group $P2_1/c$ with two molecules in the unit cell. Each molecule of **8** has a crystallographic centre of inversion. A view of the molecule with the atom labelling for the unique atoms in the asymmetric unit, as used in this study, is shown in Fig. 2. Atomic coordinates and thermal parameters are listed in Table 1. No unusually short intermolecular contacts were observed. Relevant bond length and bond angle data are given in Tables 2 and 3. The overall geometry of **8** is similar to that observed for $[Pd_2(\eta^2;\mu_2\text{-}SCN)_2\{(PPh_2O)_2H\}_2]$ [13]. Each palladium atom dis-

TABLE 3. Interatomic angles (°) for **8** with e.s.d.s. in parentheses[a]

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| I–Pd–I′ | 85.9(1) | Pd–I–Pd′ | 94.1(1) |
| I–Pd–P(1) | 177.8(1) | I′–Pd–P(2) | 174.0(1) |
| I–Pd–P(2) | 91.2(1) | I′–Pd–P(1) | 92.1(1) |
| P(1)–Pd–P(2) | 90.9(1) | | |
| Pd–P(1)–O(1) | 116.8(1) | Pd–P(2)–O(2) | 117.6(1) |
| Pd–P(1)–C(1) | 113.3(1) | Pd–P(2)–C(13) | 109.9(1) |
| Pd–P(1)–C(7) | 109.9(1) | Pd–P(2)–C(19) | 109.6(2) |
| O(1)–P(1)–C(1) | 102.4(2) | O(2)–P(2)–C(13) | 104.4(2) |
| O(1)–P(1)–C(7) | 105.5(2) | O(2)–P(2)–C(19) | 105.7(2) |
| C(1)–P(1)–C(7) | 108.2(2) | C(13)–P(2)–C(19) | 109.3(2) |
| P(1)–C(1)–C(2) | 115.9(4) | P(2)–C(13)–C(14) | 124.3(4) |
| P(1)–C(1)–C(6) | 125.3(4) | P(2)–C(13)–C(18) | 116.8(3) |
| C(2)–C(1)–C(6) | 118.8(5) | C(14)–C(13)–C(18) | 119.0(4) |
| C(1)–C(2)–C(3) | 120.4(7) | C(13)–C(14)–C(15) | 119.8(5) |
| C(2)–C(3)–C(4) | 119.4(7) | C(14)–C(15)–C(16) | 120.6(5) |
| C(3)–C(4)–C(5) | 120.5(6) | C(15)–C(16)–C(17) | 119.8(5) |
| C(4)–C(5)–C(6) | 120.7(7) | C(16)–C(17)–C(18) | 120.8(5) |
| C(1)–C(6)–C(5) | 120.1(6) | C(13)–C(18)–C(17) | 120.1(5) |
| P(1)–C(7)–C(8) | 120.0(4) | P(2)–C(19)–C(20) | 123.7(4) |
| P(1)–C(7)–C(12) | 120.5(3) | P(2)–C(19)–C(24) | 118.0(4) |
| C(8)–C(7)–C(12) | 118.9(4) | C(20)–C(19)–C(24) | 117.8(5) |
| C(7)–C(8)–C(9) | 121.2(5) | C(19)–C(20)–C(21) | 121.4(5) |
| C(8)–C(9)–C(10) | 119.4(5) | C(20)–C(21)–C(22) | 119.5(6) |
| C(9)–C(10)–C(11) | 120.4(5) | C(21)–C(22)–C(23) | 120.6(6) |
| C(10)–C(11)–C(12) | 119.5(5) | C(22)–C(23)–C(24) | 120.4(7) |
| C(7)–C(12)–C(11) | 120.6(5) | C(19)–C(24)–C(23) | 120.3(6) |

[a]Primes refer to the symmetry transformation $1-x$, $1-y$, $1-z$.

plays square planar coordination with two *cis*-coordinated phosphidoxo ligands and two bridging iodo ligands. The Pd–P distances (2.273(1) and 2.272(1) Å) are typical of those observed in other square planar palladium(II) complexes* and the Pd–I distances of 2.709(1) and 2.700(1) Å (both *trans* to P) compare with 2.662(1) (*trans* to P) and 2.723(1) (*trans* to C) Å in $[\{Pd(\mu\text{-}I)P(o\text{-}MeC_6H_4)_2\text{-}o\text{-}C_6H_4CH_2\}_2]$ [17] and 2.592(1) Å (*trans* to I) in $[Pd_2I_6]^{2-}$ [18] the two other compounds with iodo ligands bridging two non-bonded palladium atoms that have been structurally characterised. The angles around the $Pd_2I_2$ rhombus are similar to those in $[\{Pd(\mu\text{-}I)P(o\text{-}MeC_6H_4)_2\text{-}o\text{-}C_6H_4CH_2\}_2]$ [17]. Strong, symmetrical O–H–O hydrogen bonding between the phosphidoxo groups is suggested by the following evidence. (i) The bridging hydrogen atom of the $Ph_2PO{-}H{-}OPPh_2$ units was found to be symmetrically disposed between the two phosphidoxo oxygen atoms. (ii) The short O–O distance (2.375(5) Å) in **8** compares favourably with that found in $[Pd_2(\eta^2;\mu_2\text{-}SCN)_2\{(PPh_2O)_2H\}_2]$ (2.421(7) Å) [13]. These distances are both in the range typical for strong, symmetrical O–H–O hydrogen bonding [19, 13a]. (iii) The independent pair of P–O bond distances, P(1)–O(1) 1.553(3) Å and P(2)–O(2) 1.549(3) Å, are equivalent within the error of the determination. This clearly demonstrates the lack of any asymmetry in **8**. (iv) There are no bands in the $\nu$(O–H) region of the infrared spectrum (in symmetric O–H–O hydrogen bound systems the O–H–O bands typically occur lower than 1800 $cm^{-1}$ [13a]).

*For example see discussion of Pd–P distances in refs. 3, 13–15.

## Supplementary materials

Tables of fractional coordinates, isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond angles, bond distances, torsional angles, and observed and calculated structure factors for $[Pd_2(\mu\text{-}I)_2\text{-}\{(PPh_2O)_2H\}_2]$ (**8**) are available on request from author D.C.C.

## References

1 S. B. Colbran, D. C. Craig and S. B. Sembiring, *XXVII Int. Coord. Chem. Conf., Broadbeach, Australia, 1989,* Abstr. W99; *Inorg. Chem.*, to be published.

2 F. Ramirez, D. Rhum and C. P. Smith, *Tetrahedron, 21* (1965) 1941.

3 H. D. Empsall, P. N. Heys, W. S. McDonald, M. C. Norton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* (1978) 1119; H. D. Empsall, P. N. Heys, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* (1978) 257; H. D. Empsall, E. M. Hyde and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* (1975) 1691; H. D. Empsall, E. M. Hyde C. E. Jones and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* (1974) 1980.

4 M. V. Bhatt and S. U. Kulkarni, *Synthesis,* (1983) 249.

5 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-Ray Crystallography,* Vol. 4, Kynoch Press, Birmingham, U.K., 1974.

6 P. Main, *MULTAN80,* University of York, U.K., 1980.

7 W. R. Busing, K. O. Martin and H. A. Levy, *ORFLS,* Oak Ridge National Laboratory, TN, U.S.A., 1962.

8 C. K. Johnson, *ORTEP-II,* Oak Ridge National Laboratory, TN, U.S.A., 1976.

9 A. T. Hutton and C. P. Morely, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Inorganic Chemistry,* Vol. 5, Pergamon, Oxford, 1987, Ch. 51.9, p. 1157.

10 J. A. Rahn, M. S. Holt and J. H. Nelson, *Polyhedron, 8* (1989) 897, and refs. therein.

11 P. S. Pregosin in J. G. Verkade and L. D. Quin (eds.), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis,* VCH, Deerfield Beach, FL, 1987, Ch. 14, p. 465.

12 C. E. Jones, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.,* (1974) 992.

13 (a) A. J. Carty, S. E. Jacobson, R. T. Simpson and N. J. Taylor, *J. Am. Chem. Soc., 97* (1975) 7254; (b) D. V. Naik, G. J. Palenik, S. Jacobson and A. J. Carty, *J. Am. Chem. Soc., 96* (1974) 2286.

14 P. Bergamini, S. Sostero, O. Traverso, T. J. Kemp and P. G. Pringle, *J. Chem. Soc., Dalton Trans.,* (1989) 2017.

15 E. H. Wong and F. C. Bradley, *Inorg. Chem., 20* (1981) 2333; K. R. Dixon and A. D. Rattray, *Can. J. Chem., 49* (1971) 3997.

16 M. C. Cornock, R. O. Gould, C. L. Jones and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.,* (1977) 1307; P.-C. Kong and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.,* (1974) 187; P.-C. Kong and D. M. Roundhill, *Inorg. Chem., 11* (1972) 749.

17 A. L. Rheingold and W. C. Fultz, *Organometallics, 3* (1984) 1414.

18 F. Maassarani, M. Pfeffer and G. Le Borgne, *Organometallics, 6* (1987) 2043; F. Maassarani, M. Pfeffer and G. Le Borgne, *J. Chem. Soc., Chem. Commun.,* (1987) 565.

19 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids,* Benjamin, New York, 1968, p. 182.