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Notes

Crystal Structure and NMR Characterization of the Unexpected Product of Oxidation of $[(Ph_2PCHCH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCHCH_2)Pd^I]_2(BF_4)_2$ with Iodine: Bis(μ-iodo)bis[iodo(diphenylvinylphosphine)-palladium(II)]

Nathaniel W. Alcock,[†] **William L. Wilson,**[‡] **and John H. Nelson**[*,‡]

Departments of Chemistry, University of Warwick,
Coventry CV47AL, England, and University of Nevada,
Reno, Nevada 89557-0020

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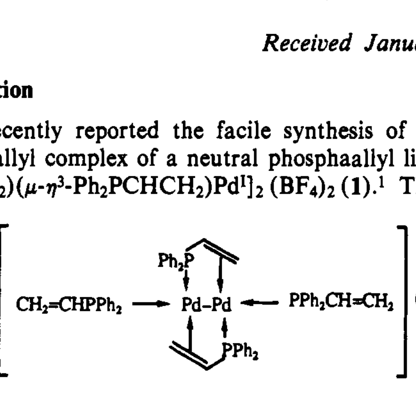
Introduction

We recently reported the facile synthesis of the first η^3-phosphaallyl complex of a neutral phosphaallyl ligand, $[(Ph_2PCHCH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCHCH_2)Pd^I]_2(BF_4)_2$ (**1**).[1] The vinylphosphine is bound to the palladium atoms in this complex in an uncommon way, and the palladium(I) oxidation state is normally not observed with monodentate phosphorus donor ligands. A ruthenium(II) complex containing this same phosphaallyl ligand was observed to react with nucleophiles either at the ruthenium or phosphorus centers depending upon the nature of the nucleophile.[2] Nucleophilic addition to phosphorus in this complex was completely unexpected and led to a ruthenium vinyl complex by migration of a vinyl group from phosphorus to ruthenium. The palladium(I) complexes $Pd_2(\mu\text{–}dppm)_2X_2$ undergo oxidative addition reactions with halogens (Cl_2, Br_2, I_2) to from $Pd_2(\mu\text{–}dppm)_2X_4$, which subsequently rearrange by bridge cleavage to yield $Pd(dppm)X_2$.[3]



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Because of the unusual nature of complex **1**, we have begun to study its chemical reactivity and report herein its reaction with molecular iodine.

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were used as received. Diphenylvinylphosphine was obtained from Organometallics, Inc. Compound **1** was prepared as previously described.[1] Melting points were determined on a Mel-Temp apparatus and are uncorrected. NMR spectra were obtained as previously described.[2] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

(B) Synthesis of *sym-trans*-$[(Ph_2PCHCH_2)PdI_2]_2$ (2). To a solution containing 0.500 g (0.4049 mmol) of **1** in 50 mL of dichloromethane was added 0.2055 g (0.8097 mmol) of I_2 under nitrogen. The resulting dark red-brown solution was stirred magnetically for 4 h at ambient temperature, and then the solution volume was reduced to about 10 mL on a rotary evaporator. Addition of diethyl ether produced dark red-brown crystals that were isolated by filtration, washed with diethyl ether, and recrystallized from CH_2Cl_2/Et_2O to yield 0.4066 g (87.8%) of *sym-trans*-$[(Ph_2PCHCH_2)PdI_2]_2$, mp 212–215 °C with decomposition. Anal. Calcd for $C_{28}H_{26}I_4P_2Pd_2$: C, 29.38; H, 2.27. Found: C, 29.21; H, 2.35. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.45. ^1H NMR ($CDCl_3$): δ 5.58 (dd, $^3J(PH) = 20.74$ Hz, $^3J(H_aH_c) = 18.18$ Hz, 2H, H_c), 6.10 (dd, $^3J(PH) = 42.37$ Hz, $^3J(H_aH_b) = 12.02$ Hz, 2H, H_b), 7.12 (ddd, $^2J(PH) = 24.04$ Hz, $^3J(H_aH_c) = 18.18$ Hz, $^3J(H_aH_b) = 12.02$ Hz, 2H, H_a), 7.4–7.7 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 128.42 (d, $^3J(PC) = 11.49$ Hz, C_m), 128.49 (d, $^3J(PC) = 11.19$ Hz, C_m'), 129.58 (d, $^1J(PC) = 57.44$ Hz, C_i), 131.57 (s, C_p), 132.91 (d, $^1J(PC) = 53.66$ Hz, C_α), 134.33 (d, $^2J(PC) = 10.43$ Hz, C_o), 134.41 (d, $^2J(PC) = 10.05$ Hz, C_o'), 134.73 (s, C_β).

Table I. Crystallographic Data for 2

composn: $C_{28}H_{26}I_4P_2Pd$(**2**)	$Z = 4$
fw = 1144.8	$d_{calc} = 2.23$ g cm^{-3}
space group: $P\bar{1}$	$T = 17$ °C
a = 13.683(6) Å	λ(Mo Kα) = 0.710 69 Å
b = 15.319(8) Å	$\mu = 47.4$ cm^{-1}
c = 16.366(7) Å	transm factor range: 0.42–0.70
$\alpha = 89.10(4)°$	no. of obsd rfclns: 4597 [$I \geq 2\sigma(I)$]
$\beta = 88.15(4)°$	$R_F{}^a = 0.076$
$\gamma = 81.85(4)°$	$R_w(F)^b = 0.085$
$V = 3409(3)$ Å^3	

[a] $R_F = \sum w(|F_o| - |F_c|)^2$ with $\sigma^2(F)^2 = \sigma^2(\text{counts}) + (pI)^2$. [b] $R_w(F) = \sum w[(|F_o|) - |F_c|^2)/\sum w|F_o|^2]^{1/2}$.

(C) X-ray Data Collection and Processing. Dark red-brown plates of **2** were obtained from CH_2Cl_2/Et_2O. Crystal data and details of data collection are given in Table I. Data were collected with a Nicolet P2$_1$ four-circle diffractometer in the ω–2θ mode. Maximum 2θ was 50° (partial data only in the 45–50° range due to relatively weak diffraction) with scan range ±1.2° (2θ) around the $K_{\alpha 1} - K_{\alpha 2}$ angles and scan speed 6–29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections and showed a slight decrease (6% on I) during data collection. The data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least-squares fit to 18 reflections ($20 < 2\theta < 22°$). Reflections were processed using profile analysis to give 9281 unique reflections, of which 4597 were considered observed ($I/\sigma(I) \geq 2.0$). These were corrected for Lorentz, polarization, and absorption effects (by the Gaussian method). No systematic absences were found. Space group $P\bar{1}$ was assumed and shown to be correct by successful refinement. Initial attempts at structure solution by Patterson methods failed, presumably because the heavy atoms in both molecules are virtually coplanar, with many duplicate vectors. The structure was solved with some difficulty by using SHELTXL (TREF)[4] to locate the heavy atoms. The light atoms were then found on successive Fourier syntheses. Anisotropic temperature factors were used for non-H atoms not involved in disorder. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.08$ Å^2, inserted at calculated positions and not refined. Final refinement was on F by least-squares methods refining 345 parameters.

There are two independent molecules in the asymmetric unit. Two phenyl rings in molecule two had very high thermal parameters and appear to be disordered (C(207)–C(212) and C(221)–C(226). Their C atoms (apart from the ipso atom) were given 0.5 occupancy parameters, and they were held as rigid hexagons, C–C = 1.395 Å; their H atoms were not included. The residual electron density near them suggested that each ring also took up several minor positions, but these were not modeled. Largest positive and negative peaks on a final difference Fourier synthesis were of height ±2 e Å^{-3}. All large peaks were close to I or Pd, with some smaller residuals in the vicinity of the disordered phenyl rings. A weighting scheme of the form $1/(\sigma^2(F) + 0.005F^2)$ was used and shown to be satisfactory by weight analysis. The relatively large R value is understandable in light of the disorder observed. Computing was done with SHELTXL PLUS[4] on a DEC Microvax-II computer. Scattering factors

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[*] To whom correspondence should be addressed.

[†] University of Warwick.

[‡] University of Nevada.

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Table II. Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[(Ph_2PCHCH_2)PdI_2]_2$ (**2**)[a]

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
I(11)	2057.3(20)	968.3(13)	7679.3(11)	69(1)	I(21)	1847.4(18)	6961.0(13)	2743.5(10)	58(1)
I(12)	2049.2(17)	1837.4(12)	9674.9(10)	52(1)	I(22)	1867.3(18)	6004.1(13)	4721.6(11)	61(1)
I(13)	2257.1(21)	4054.3(14)	8816.3(13)	76(1)	I(23)	2244(3)	9093(2)	3584(2)	100(1)
I(14)	2076.4(23)	−1280.6(14)	8522.4(13)	85(1)	I(24)	2279(3)	3786(2)	3867(2)	134(2)
Pd(11)	2088.5(18)	2553.1(14)	8186.6(12)	45(1)	Pd(21)	2050.6(19)	5336.5(15)	3224.6(12)	50(1)
Pd(12)	2052.5(19)	248.7(14)	9163.8(12)	49(1)	Pd(22)	2009.9(19)	7591.9(15)	4323.2(13)	52(1)
P(11)	2124(6)	3149(5)	6924(4)	45(3)	P(21)	2299(7)	4779(6)	1958(4)	57(3)
P(12)	2112(6)	−398(5)	10402(4)	50(3)	P(22)	2111(7)	8130(7)	5492(5)	72(4)
C(101)	1863(22)	2462(17)	6122(16)	46(7)	C(201)	1857(23)	5558(18)	1143(17)	52(8)
C(102)	2590(23)	2102(17)	5533(16)	51(8)	C(202)	816(29)	5836(23)	1073(23)	91(12)
C(103)	2284(30)	1588(23)	4971(22)	87(12)	C(203)	476(27)	6437(21)	527(19)	71(10)
C(104)	1450(31)	1385(25)	4932(24)	96(13)	C(204)	1117(29)	6696(23)	−51(22)	85(11)
C(105)	700(28)	1694(21)	5509(20)	80(11)	C(205)	2108(30)	6493(24)	−46(23)	95(13)
C(106)	971(23)	2243(18)	6089(18)	56(8)	C(206)	2515(34)	5844(25)	574(24)	110(14)
C(107)	3312(22)	3482(18)	6673(16)	49(8)	C(207)	3637(20)	4511(22)	1746(20)	109(14)
C(108)	4137(25)	2921(21)	6867(19)	68(9)	C(208)	3998(20)	3902(22)	1148(20)	48(15)
C(109)	5102(30)	3153(25)	6704(22)	93(12)	C(209)	4970(20)	3861(22)	850(20)	127(32)
C(110)	5096(31)	3909(24)	6239(22)	95(12)	C(210)	5580(20)	4428(22)	1149(20)	99(26)
C(111)	4320(33)	4490(29)	5998(25)	115(15)	C(211)	5219(20)	5037(22)	1747(20)	65(18)
C(112)	3401(26)	4171(20)	6248(19)	69(10)	C(212)	4247(20)	5078(22)	2045(20)	39(13)
C(113)	1255(22)	4138(19)	6808(18)	57(8)	C(213)	1782(28)	3820(25)	1768(23)	95(13)
C(114)	732(26)	4359(24)	6191(21)	90(12)	C(214)	1237(24)	3682(22)	1161(19)	74(10)
C(115)	1965(26)	403(20)	11252(19)	65(9)	C(215)	1688(23)	7364(18)	6352(17)	53(8)
C(116)	2799(29)	502(23)	11640(21)	85(11)	C(216)	739(31)	7185(24)	6341(24)	98(13)
C(117)	2661(36)	1145(27)	12375(26)	117(15)	C(217)	414(37)	6616(27)	6975(26)	122(16)
C(118)	1763(30)	1512(24)	12483(23)	86(12)	C(218)	1136(35)	6315(28)	7511(28)	118(15)
C(119)	997(32)	1398(24)	12100(22)	95(13)	C(219)	2038(27)	6429(21)	7532(20)	71(10)
C(120)	1045(27)	832(21)	11430(20)	73(10)	C(220)	2465(37)	6940(28)	6963(26)	127(16)
C(121)	3243(22)	−1083(18)	10504(17)	50(8)	C(221)	3332(25)	8203(31)	5733(26)	175(23)
C(122)	4071(29)	−893(24)	10115(23)	93(12)	C(222)	3597(25)	8922(31)	6137(26)	118(30)
C(123)	5020(34)	−1389(27)	10262(26)	113(14)	C(223)	4573(25)	8923(31)	6358(26)	160(41)
C(124)	5135(38)	−2047(29)	10824(27)	125(16)	C(224)	5285(25)	8205(31)	6174(26)	103(27)
C(125)	4309(30)	−2318(25)	11108(23)	95(12)	C(225)	5020(25)	7486(31)	5770(26)	86(22)
C(126)	3343(28)	−1831(21)	11035(20)	77(10)	C(226)	4044(25)	7485(31)	5549(26)	42(14)
C(127)	1163(22)	−1037(18)	10627(18)	57(8)	C(227)	1407(25)	9157(21)	5667(20)	73(10)
C(128)	685(26)	−1194(21)	11294(20)	83(11)	C(228)	832(25)	9358(22)	6329(20)	80(11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) for $[(Ph_2PCHCH_2)PdI_2]_2$ (2)

I(11)–Pd(11)	2.595(3)	I(11)–Pd(12)	2.655(3)
I(12)–Pd(11)	2.660(3)	I(12)–Pd(12)	2.596(3)
I(13)–Pd(11)	2.587(3)	I(14)–Pd(12)	2.588(3)
Pd(11)–P(11)	2.249(7)	Pd(12)–P(12)	2.242(7)
P(11)–C(101)	1.775(29)	P(11)–C(107)	1.806(32)
P(11)–C(113)	1.805(28)	P(12)–C(115)	1.860(32)
P(12)–C(121)	1.756(29)	P(12)–C(127)	1.763(33)
I(21)–Pd(21)	2.589(3)	I(21)–Pd(22)	2.664(3)
I(22)–Pd(21)	2.662(3)	I(22)–Pd(22)	2.591(3)
I(23)–Pd(22)	2.583(4)	I(24)–Pd(21)	2.575(4)
Pd(21)–P(21)	2.253(8)	Pd(22)–P(22)	2.249(9)
P(21)–C(201)	1.838(28)	P(21)–C(207)	1.841(28)
P(21)–C(213)	1.762(42)	P(22)–C(215)	1.947(30)
P(22)–C(221)	1.749(37)	P(22)–C(227)	1.753(32)

Table IV. Selected Bond Angles (deg) for $[(Ph_2PCHCH_2)PdI_2]_2$ (2)

Pd(11)–I(11)–Pd(12)	95.1(1)	Pd(11)–I(12)–Pd(112)	95.0(1)
I(11)–Pd(11)–I(12)	84.9(1)	I(11)–Pd(11)–I(13)	173.5(1)
I(12)–Pd(11)–I(13)	90.1(1)	I(11)–Pd(11)–P(11)	94.7(2)
I(12)–Pd(11)–P(11)	179.6(2)	I(13)–Pd(11)–P(11)	90.3(2)
I(11)–Pd(12)–I(12)	85.0(1)	I(11)–Pd(12)–I(14)	89.9(1)
I(12)–Pd(12)–I(14)	174.8(1)	I(11)–Pd(12)–P(12)	177.4(2)
I(12)–Pd(12)–P(12)	96.4(2)	I(14)–Pd(12)–P(12)	88.7(2)
Pd(21)–I(21)–Pd(22)	94.5(1)	Pd(21)–I(22)–Pd(22)	94.5(1)
I(21)–Pd(21)–I(22)	84.6(1)	I(21)–Pd(21)–I(24)	173.5(1)
I(22)–Pd(21)–I(24)	89.0(1)	I(21)–Pd(21)–P(21)	95.0(2)
I(22)–Pd(21)–P(21)	176.7(3)	I(24)–Pd(21)–P(21)	91.3(2)
I(21)–Pd(22)–I(22)	84.5(1)	I(21)–Pd(22)–I(23)	89.5(1)
I(22)–Pd(22)–I(23)	173.1(1)	I(21)–Pd(22)–P(22)	178.8(3)
I(22)–Pd(22)–P(22)	95.4(3)	I(23)–Pd(22)–P(22)	90.7(3)

in the analytical form and anomalous dispersion factors were taken from ref 5. Final atom coordinates and selected bond lengths and angles are given in Tables II–IV, respectively.

Results and Discussion

The palladium(I) phosphaallyl complex, **1**, was expected to undergo oxidative addition with molecular iodine to yield a compound containing a 2:1 phosphine:palladium ratio as for example $[(Ph_2PCHCH_2)_2PdI(BF_4)]$, $[(Ph_2PCHCH_2)_2(\mu\text{-}I)\text{-}Pd]_2(BF_4)_2$, or *trans*-$(Ph_2PCHCH_2)_2PdI_2$. The latter has been previously characterized,[6] while the former are unknown. Reaction of **1** with an excess of I_2 in CH_2Cl_2 at ambient temperature yielded a deep red-brown solution that exhibited ^{31}P resonances at δ 26.45 and 29.21 ppm in an approximately 1:1 ratio. The latter is due to $Ph_2P(O)CH{=}CH_2$, which was probably formed by hydrolysis of $Ph_2P(CH{=}CH_2)I_2$ by adventitious water.[7] The former is not due to *trans*-$(Ph_2PCHCH_2)_2PdI_2$ as the $^{31}P\{^1H\}$ chemical shift of this complex is 4.7 ppm.[5] The large downfield chemical shift of the 26.45 ppm resonance relative to that of $(Ph_2PCHCH_2)_2PdI_2$ suggested a dimeric iodide-bridged species[8,9] with the phosphines *trans* to a bridging iodide. Dark red-brown crystals were isolated from this solution by concentration and addition of diethyl ether. The first-order nature of the ^1H and $^{13}C\{^1H\}$ NMR spectra of the isolated crystals suggested the absence of two symmetry-equivalent phosphines coordinated to the same palladium center.[6]

The elemental analyses, taken together with the NMR spectral data, suggested that the products of reaction 1 are the palladium(II) iodide-bridged dimer; $[(Ph_2PCHCH_2)PdI(\mu\text{-}I)]_2$ (**2**), and $Ph_2P(O)CH{=}CH_2$. Were 2 mol of the phosphine not oxidized by reaction with I_2, the phosphine would be expected to react with **2** to form $(Ph_2PCHCH_2)_2PdI_2$.[10]

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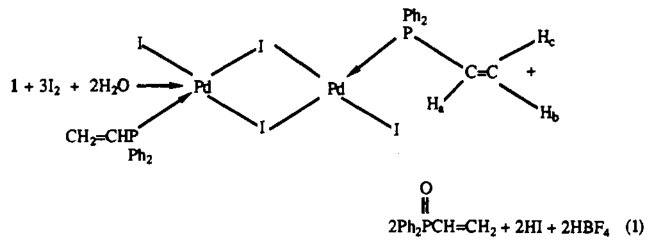
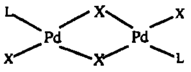
(5) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.



$$2Ph_2\overset{O}{\overset{\|}{P}}CH{=}CH_2 + 2HI + 2HBF_4 \quad (1)$$

The structure of **2** was established unequivocally by X-ray crystallography (Figure 1). The structure consists of two nearly equivalent molecules in the asymmetric unit, both of which are the symmetric *trans* isomer, A. Of the three possible isomers,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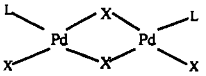
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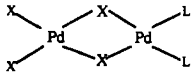
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A–C, only isomer A has been previously observed.[11] Selected bond lengths and angles are listed in Tables III and IV. The molecule contains unsymmetrically bridged iodides. The Pd–I_b distances trans to the phosphines (2.658(3) Å, average) are significantly longer than the Pd–I_b distances trans to the terminal iodides (2.596(3) Å, average) and the Pd–I_t distances (2.588(3) Å, average). The $Pd_2I_{2(b)}$ unit is a rhombus with considerable difference in the I_bPdI_b (84.9(1)°, average) and PdI_bPd (95(1)°, average) angles. The Pd–P distances (2.246(7) Å, average) are equal.

Similar structures have been reported for $[PdCl_2(C_2H_4)]_2$,[12] $[PdBr_2(Me_2S)]_2$,[13] $[Pd(Me_3As)\ Br_2]_2$,[14] and $[Pd(C_6H_5CHCH_2)Cl_2]_2$.[15] The Pd–P distances in **2** are considerably shorter than those in *trans*-$(Me_2PPh)_2PdI_2$ (2.592(3) Å, yellow isomer, or 2.638(3) and 2.619(3) Å, red isomer).[16,17] The short Pd–P bonds in **2** are consistent with the large downfield ^{31}P chemical shift compared to *trans*-$(Ph_2PCHCH_2)_2PdI_2$. Similar large downfield ^{31}P chemical shifts are observed for the halide-bridged species $[(R_3P)HgX_2]_2$ compared to $(R_3P)_2HgX_2$.[18]

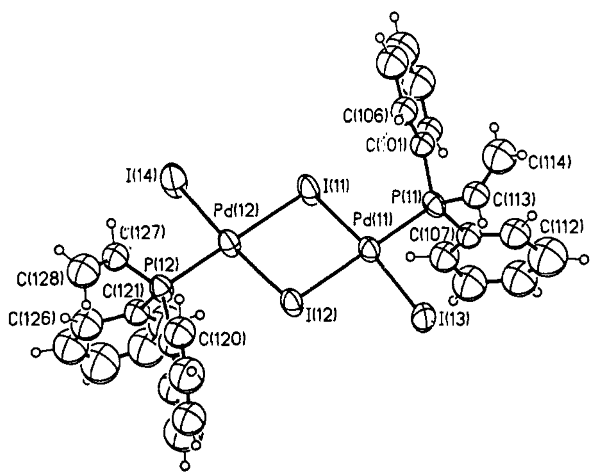

Figure 1. View of molecule 1 of **2** showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have an arbitrary radius of 0.1 Å.

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Supplementary Material Available: Listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*) (5 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors (34 pages) are available from the authors.

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