Synthesis and Chemistry of Some Palladacyclopentanes

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The palladacyclopentane complexes $[Pd(CH_2CH_2CH_2CH_2)L_2]$ [(1) L_2 = 1,2-bis(diphenylphosphino)ethane (dppe); (2) L_2 = *NNN'N'*-tetramethylethylenediamine (tmen)] have been prepared by reaction of the corresponding dichlorides with an ether solution of 1,4-dilithiobutane. Compound (2) participates in substitution reactions of tmen with various ligands [dppe, 2,2'-bipyridyl (bipy), or PPh_3] affording (1), $[Pd(CH_2CH_2CH_2CH_2)(bipy)]$ (3), and $[Pd(CH_2CH_2CH_2CH_2)(PPh_3)_2]$ (4) respectively. The palladium–carbon bonds of these compounds are easily cleaved by HCl and Br_2 to give n-butane and 1,4-dibromobutane as the organic products. Treatment of (1) with CO does not result in carbonylation products; by contrast, (2)—(4) react to give cyclopentanone. Compound (1) and some isostructural linear palladium dialkyls react with SO_2 to give the corresponding *S*-bonded disulphinates. Compounds (1), (3), and (4) undergo ready hydride abstraction by the trityl cation to give the η^3-1-methylallyl complexes, $[Pd(\eta^3\text{-}CH_2CHCHMe)L_2][BF_4]$.

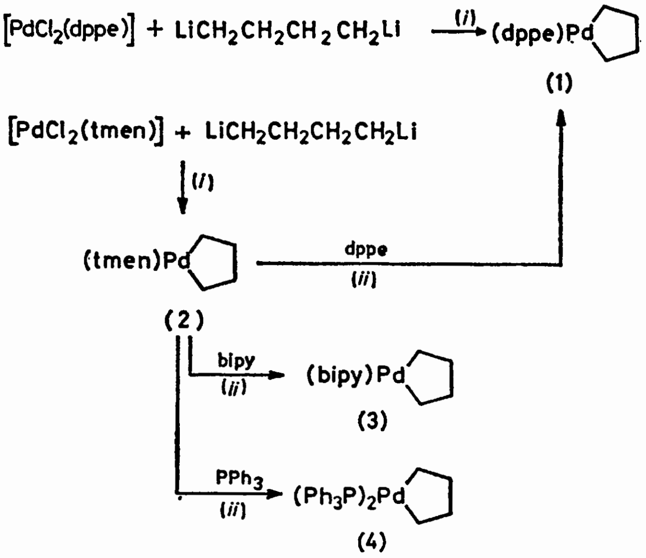
In recent years there has been intense interest in the chemistry of transition-metal metallacycloalkanes from the point of view of comparing their properties and stability with those of analogous linear dialkyls,[1] and of testing the validity of the hypothesis which locks the metallacycles into the chain of events describing several transition-metal-catalyzed reactions.[2] So far the amount of work that has been done in this field has produced a number of reports concerning the synthesis and properties of metallacycles of various transition metals. Despite these efforts little information is available about the reactivity and possible peculiarities of this class of alkyls in reactions typical of linear alkyls.

In this context we have started a study of the synthesis and reactivity of some Group 8 metallacycles.[3] More recently our interest was focused on the chemistry of palladacyclopentane derivatives and a preliminary account has already been made.[4] We now describe the details and some extensions of these studies.

RESULTS AND DISCUSSION

Preparation of Palladacyclopentanes.—Scheme 1 outlines the reactions employed for the preparation of the palladacyclopentane derivatives (1)—(4). Treatment of a suspension of $[PdCl_2(dppe)]$[dppe = 1,2-bis(diphenylphosphino)ethane] in diethyl ether with 1,4-dilithiobutane at −70 °C gave off-white crystals which the data in the Table show to be the metallacyclopentane $[Pd(CH_2CH_2CH_2CH_2)(dppe)]$ (1). Compound (1) is soluble in aromatic solvents and the solutions are thermally stable at room temperature. Analogously, by treating a solution of $[PdCl_2(tmen)]$ (tmen = *NNN'N'*-tetramethylethylenediamine) in ether with 1,4-dilithiobutane, white crystals of $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (2) were eventually obtained. Compound (2) is soluble in aliphatic and aromatic solvents, but the solutions are thermally unstable even at room temperature. The tmen ligand is easily displaced from complex (2) by a number of ligands. Thus, treatment of pentane solutions of (2) with dppe, bipy (2,2'-bipyridyl), or PPh_3 gave almost immediately and quantitatively the metallacyclopentanes (1), (3), and (4), respectively. Many attempts to prepare (3) and (4) by the usual procedure of alkylation of the corresponding dichloro-compounds with 1,4-dilithiobutane were unsuccessful. Compound (3) is soluble in acetone, (4) in aromatic solvents. Their thermal stability in solution is higher than that of (2).

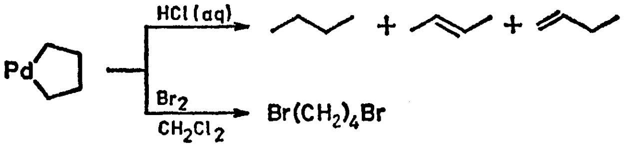
The ^1H n.m.r. spectra of (1)—(3) (Table) are consistent with a metallacyclic structure showing, in addition to the ligand resonances, two multiplets in the aliphatic region attributable to the α- and β-methylenes of the ring. The spectrum of (4) is unusual in this respect showing just one broad multiplet whose integrated area corresponds to all the eight hydrogens of the tetramethylene moiety.



SCHEME 1 (*i*) In diethyl ether, −70 °C, Li : Pd = 6 : 1; (*ii*) in pentane, room temperature

The structural assignments were confirmed by treating (1)—(4) with HCl or Br_2. Reaction with HCl gave substantial amounts of n-butane and traces of n-butenes [larger amounts of n-butenes, 30%, were found in the case of (1)]. In the cases of (1) and (4), the corresponding dichlorides were isolated. Bromination resulted in the production of 1,4-dibromobutane (Scheme 2).

Reactions of Palladacyclopentanes.—(*a*) *With carbon monoxide.* The reaction is dependent on the nature of the supporting ligands. The dppe compound (1) does not react with CO at atmospheric pressure and room temperature; decomposition products (C_4 hydrocarbons) were observed when the reaction was carried out at higher temperatures. In contrast, metallacycles (2)—(4) react smoothly with CO to produce cyclopentanone and an unidentified organic compound with higher retention time in the chromatographic analysis. Formation of metallic palladium was also observed (Scheme 3). The different behaviour of the dppe and triphenylphosphine complexes had already been observed for nickelacyclopentanes and was attributed to the reluctance of the dppe complex to form the five-co-ordinated complex with a co-ordinated CO molecule.[5]



SCHEME 2

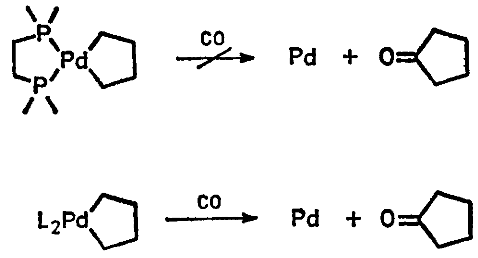
(*b*) *With sulphur dioxide.* Compounds (1)—(4) react with SO_2 in a way which is strongly dependent on the nature of the supporting ligands. Only in the case of (1) did the reaction proceed cleanly, while with complexes (2)—(4) the reaction appears to be more complicated and very sensitive to the experimental conditions. Because of the need for more experiments, we only describe the reaction of SO_2 with (1) and, by comparison, with two isostructural linear palladium dialkyls.

Analytical and spectroscopic data

	Compound	Colour	Analysis (%) [a]		^{1}H n.m.r. data [b]
			C	H	
(1)	$[Pd(CH_2CH_2CH_2CH_2)(dppe)]$	Cream	64.75 (64.2)	5.60 [c] (5.75)	2.13, **4**, *m*, Pd–CH_2; 2.31, **4**, *d* [J(P–H) 18], P–CH_2; 2.66, **4**, *m*, C–CH_2–C; 7.20—8.10, **20**, *m*, Ph [d]
(2)	$[Pd(CH_2CH_2CH_2CH_2)(tmen)]$	White	41.3 (43.05)	8.45 [e] (8.60)	0.9—1.6, **8**, br *m*, $(CH_2)_4$; 2.2—2.3, **16**, *m*, Me and CH_2 of tmen [f]
(3)	$[Pd(CH_2CH_2CH_2CH_2)(bipy)]$	Orange	51.4 (52.7)	4.95 (5.05)	1.72, **4**, *m*, Pd–CH_2; 2.25, **4**, *m*, C–CH_2–C; 7.42, **2**, *m*, bipy; 8.06, **4**, *m*, bipy; 8.76, **2**, *m*, bipy [g]
(4)	$[Pd(CH_2CH_2CH_2CH_2)(PPh_3)_2]$	Cream	70.5 (69.9)	5.55 (5.55)	2.33, **8**, *m*, $(CH_2)_4$; 6.80—7.80, **30**, *m*, Ph [f]
(5)	$[Pd\{S(O)_2(CH_2)_4S(O)_2\}(dppe)]\cdot 0.5CH_2Cl_2$ [h]	Yellow	49.7 (50.1)	4.90 [i] (4.55)	2.03, **4**, *m*, C–CH_2–C; 2.23, **4**, *d* [J(P–H) 20], P–CH_2; 3.30, **4**, *m*, S–CH_2; 5.32, **1**, *s*, CH_2Cl_2; 7.30—8.00, **20**, *m*, Ph [g,j]
(6)	$[Pd\{S(O)_2Me\}_2(dppe)]\cdot 0.5CH_2Cl_2$ [k]	Yellow	46.7 (46.1)	4.15 [l] (4.45)	2.30, **4**, *d* [J(P–H) 22], P–CH_2; 2.60, **6**, *s*, S–Me; 5.30, **1**, *s*, CH_2Cl_2; 7.30—8.20, **20**, *m*, Ph [g]
(7)	$[PdBu^n{}_2(dppe)]$	Cream	66.35 (65.95)	7.00 (6.80)	0.94, **6**, *t* (J 6), Me; 1.20 and 2.20, **12**, *m*, CH_2 of Bu^n; 1.85, **4**, *d* [J(P–H) 18], P–CH_2; 7.40 and 7.80, **20**, *m*, Ph [f]
(8)	$[Pd\{S(O)_2Bu^n\}_2(dppe)]\cdot CH_2Cl_2$ [m]	Yellow	50.55 (50.5)	5.25 (5.35)	
(9)	$[Pd(\eta^3\text{-}CH_2CHCHMe)(dppe)][BF_4]$	Cream	54.75 (55.7)	4.90 (4.80)	1.66, **3**, *m*, Me; 2.59, **4**, *d* [J(P–H) 22], P–CH_2; 2.60—3.70, **1**, br *m*, H_a; 4.53, **2**, br *m*, H_b and H_s; 5.66, **1**, *m*, H_c; 7.23—8.00, **20**, *m*, Ph [g,n]
(10)	$[Pd(\eta^3\text{-}CH_2CHCHMe)(bipy)][BF_4]$	Orange	41.35 (41.55)	4.00 (3.75)	1.60, **3**, *d* (J 6), Me; 3.30—3.80, **1**, br *m*, H_a; 3.90—4.60, **2**, *m*, H_b and H_s; 5.92, **1**, *m*, H_c; 7.20—8.85, **8**, *m*, bipy [g,n]
(11)	$[Pd(\eta^3\text{-}CH_2CHCHMe)(PPh_3)_2][BF_4]$	Yellow	61.3 (62.15)	4.95 (4.80)	1.06, **3**, *m*, Me; 3.10—3.77, **2**, *m*, H_a and H_b (or H_s); 4.53, **1**, *m*, H_s (or H_b); 5.87; **1**, *m*, H_c; 6.90—8.00, **30**, *m*, Ph [g,n]

[a] Calculated values are given in parentheses. [b] Given as chemical shift (δ), **relative intensity**, *multiplicity* (J in Hz), assignment. [c] M in benzene (by cryoscopy) = 559 (calc.: 561). [d] In C_5D_5N. [e] Mass spectrum: *m/e* 278, *P* for ^{106}Pd. [f] In C_6D_6. [g] In $CDCl_3$. [h] Infrared bands at 1 178 and 1 026 cm^{-1} (SO_2) (KBr disc). [i] S, 8.45 (8.75%). [j] Carbon-13 n.m.r. spectrum in $CDCl_3$: 25.00, *s*, carbon atoms in β position from S; 28.91, *t* [J(^{13}C–^{31}P) 22], P–C; 72.26, *t* [J(^{13}C–^{31}P) 8.63], S–C; and 129.45—134.87 p.p.m., complex pattern due to phenyl carbons. [k] Infrared bands at 1 175 and 1 036 cm^{-1} (SO_2) (KBr disc). [l] S, 8.90 (9.10); Cl, 4.30 (5.25%). [m] Infrared bands at 1 175 and 1 040 cm^{-1} (SO_2) (KBr disc). [n] H_a = *anti*-H, H_b = C*H*Me, H_s = *syn*-H, H_c = central H.

Compound (1) reacts rapidly with sulphur dioxide (no solvent) at low temperatures to give a cyclic disulphinate compound, $[Pd\{S(O)_2(CH_2)_4S(O)_2\}(dppe)]\cdot 0.5CH_2Cl_2$ (5). The i.r. spectrum shows (in addition to bands due to co-ordinated dppe) strong bands at 1 175 [$\nu_{asym}(SO_2)$] and 1 040 cm^{-1} [$\nu_{sym}(SO_2)$]. These bands are generally associated to an *S*-bonded sulphinate mode of linkage and in particular are close to those observed for some *S*-bonded sulphinate derivatives of palladium(II).[6]



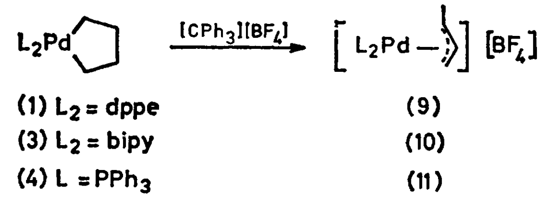
SCHEME 3 L = PPh_3; L_2 = bipy or tmen

The ^{1}H n.m.r. spectrum is consistent with the proposed formulation, showing only two types of methylene groups (those adjacent to the SO_2 groups giving resonances at low field, δ 3.30). This can arise only if the two molecules of SO_2 are inserted in the same way into the two palladium–carbon bonds. The ^{13}C n.m.r. spectrum confirms the above structure: the resonance assigned to the S–CH_2 groups appears as a doublet [J(P–C) 8.4 Hz], while the remaining carbon atoms of the disulphinate moiety (far from the phosphorus atoms) give a net singlet. Compound (5) tenaciously retains within its co-ordination sphere molecules of solvent (CH_2Cl_2 or $CHCl_3$) from which it is crystallized. This is to our knowledge the first example of insertion of two molecules of SO_2 into a dialkyl complex of palladium. Similar reactions have been observed for dimethylplatinum(II) derivatives giving the corresponding *S*-bonded disulphinates.[7] This seems to be a general reaction of [PdR_2(dppe)] complexes: [$PdMe_2$(dppe)] and [$PdBu^n{}_2$(dppe)] react with SO_2 analogously to (1) (Table).

The formation of *S*-bonded disulphinate derivatives is consistent with the ' soft ' characters of palladium(II) in the above complexes. Finally, the reactivity of the Pd–C bonds in these compounds towards SO_2, compared with the lack of reactivity of (1) and [$PdMe_2$(dppe)] [8] with CO, can be attributed to the different electrophilicities of the two molecules.

(*c*) *With the trityl cation.* Compound (1) reacts at room temperature with equimolar amounts of $CPh_3{}^+$ to give an ionic compound identified as the η^3-butenyl derivative (9) (Scheme 4). The i.r. spectrum shows a very intense band at 1 055 cm^{-1} attributable to the tetrafluoroborate anion. The complicated ^1H n.m.r. spectrum is consistent with the proposed formulation and is identical to that of the hexafluorophosphate salt of (9) prepared according to the literature.[9]

The tmen palladacyclopentane (2) decomposes to metallic palladium on reaction with the trityl cation; (3) and (4) react analogously to (1) to give the corresponding η^3-butenyl compounds (10) and (11), respectively (Scheme 4).



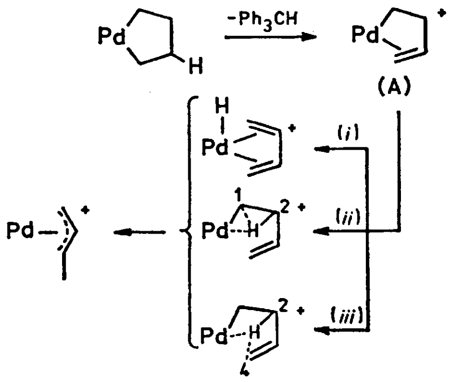
Scheme 4

All these reactions are unaffected by excess of the trityl cation. The formation of the η^3-butenyl complexes can be easily explained assuming an initial β-hydrogen abstraction by the trityl cation followed by a rapid isomerization to the stable allylic complex (Scheme 5). The labilization of β-hydrogens of σ-bonded hydrocarbon ligands is well documented in the literature and has been used to convert iron alkyls into the corresponding π-bonded alkene compounds.[10] The isomerization of the σ-but-3-enyl palladium system (A) (Scheme 5) giving the η^3-1-methylallyl palladium derivative has some precedent by analogy with the related iron system [11] [equation (1)], and in principle could occur

$$[Fe(CH_2CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)(CO)_2] \xrightarrow[-CO]{h\nu} [Fe(\eta^3\text{-}CH_2CHCHCH_3)(\eta\text{-}C_5H_5)(CO)] \quad (1)$$

through three possible pathways (Scheme 5): a hydride abstraction followed by addition of Pd–H to co-ordinated butadiene [(*i*)] or alternatively *via* a 2-1 [(*ii*)] or a 2-4 [(*iii*)] palladium-assisted hydrogen shift.

Apart from any speculation on the mechanism, the reaction of the palladacyclopentane systems with trityl cation seems to be a useful way to convert a metallacycle into an allylic compound. The reverse reaction (*i.e.* the transformation of an allylic cationic complex to a metallacyclobutane *via* nucleophilic attack by H^- or R^-) has recently been reported for tungsten and molybdenum complexes.[12] We also explored the reaction between [Pd(η^3-$CH_2CHCHCH_3$)(dppe)]$^+$ and nucleophiles such as H^- and Me^-. In all cases rapid reaction occurred giving unstable red species soluble in aromatic solvents, which were not isolated due to rapid thermal decomposition to dark materials. However, treatment of (9) with methyl-lithium gave unexpectedly [$PdMe_2$(dppe)].



Scheme 5

Conclusions.—The chemistry of these palladacyclopentanes shows no significant peculiarity with respect to the isostructural linear dialkyls, at least for the reactions studied so far. So, the reactions with CO and SO_2 follow the same pattern both for cyclic and acyclic dialkyls.

The reaction with the trityl cation deserves some comment. The behaviour in this case also resembles that of linear alkyls which react with $CPh_3{}^+$ to give co-ordinated alkenes, but the unique structure of the metallacycle yields an unsaturated hydrocarbon moiety which easily rearranges to the η^3-allylic compound.

We are planning to investigate further such transformations of metallacycles of various transition metals: we feel that, as the alkyl–alkene transformation *via* β-hydride elimination constitutes a basic process in so many stoicheiometric and catalytic reactions, the present metallacycle-π-allyl conversion may be in principle a common feature of metallacycle chemistry.

EXPERIMENTAL

All reactions and manipulations were carried out under dinitrogen. The solvents were dried and distilled. The compounds [$PdCl_2$(dppe)],[13] [$PdCl_2$(tmen)],[14] $Li(CH_2)_4Li$,[1] and [$PdMe_2$(dppe)] [15] were prepared as described. Proton n.m.r. spectra were recorded using a Varian T60 spectrometer, ^{13}C n.m.r. using a Varian XL 100 instrument. Microanalyses were by the Laboratorio di Microanalisi of Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. Infrared spectra were obtained on a Perkin-Elmer 225 instrument, mass spectra with a Varian MAT-CH7 spectrometer. G.l.c. analyses were performed on a Perkin-Elmer F30 instrument equipped with flame-ionization detectors. Melting or decomposition points were determined on a Kofler hot-stage apparatus and are uncorrected.

[1,2-*Bis*(*diphenylphosphino*)*ethane*](*tetramethylene*)-*palladium*(II), (1).—1,4-Dilithiobutane (7.4 cm³ of a 0.35 mol dm⁻³ diethyl ether solution, 2.61 mmol) was slowly added to a suspension of [$PdCl_2$(dppe)] (0.5 g, 0.86 mmol) in diethyl ether (40 cm³) at −70 °C. The suspension was stirred for 2 h, then warmed to room temperature and stirred for another 3 h. The solid formed was separated from the supernatant solution, then washed with diethyl ether (20 cm³). After removal of volatile materials the solid residue was extracted with toluene (40 cm³) and the solution filtered. To the filtrate was added pentane (30 cm³) to give cream crystals, yield 0.21 g (40%), m.p. (decomp.) 162—165 °C.

(NNN′N′-*Tetramethylethylenediamine*)(*tetramethylene*)-*palladium*(II), (2).—1,4-Dilithiobutane (10 cm³ of a 0.3 mol dm⁻³ diethyl ether solution, 2.97 mmol) was slowly added to a solution of [$PdCl_2$(tmen)] (0.43 g, 1.49 mmol) in diethyl ether (40 cm³) at −70 °C. The reaction mixture was stirred for 30 min, then the temperature was slowly raised to room temperature. After stirring for 1 h at this temperature, the volatile materials were removed under reduced pressure and the off-white residue was extracted with pentane (50 cm³). The solution was filtered and cooled (−70 °C) to give white crystals, yield 0.2 g (50%), m.p. (decomp.) 80—90 °C.

(2,2′-*Bipyridyl*)(*tetramethylene*)*palladium*(II), (3).—To a stirred solution of (2) (0.1 g, 0.36 mmol) in pentane (10 cm³) was added a solution of 2,2′-bipyridine (0.056 g, 0.36 mmol) in pentane (10 cm³). The colourless solution became orange and orange crystals precipitated. After precipitation was complete, the crystals were filtered off, washed with pentane, recrystallized from acetone, and dried *in vacuo*, yield 0.105 g (91%), m.p. (decomp.) 148 °C.

(*Tetramethylene*)*bis*(*triphenylphosphine*)*palladium*(II), (4), was similarly prepared as pale yellow crystals (by crystallization of the crude product from toluene–pentane), yield 90%, m.p. (decomp.) 97 °C. Compound (1) was also prepared (yield 95%) from the reaction of (2) with dppe.

Reactions of Metallacycles (1)—(4).—*With hydrochloric acid*. In a typical experiment, the metallacycle (50 mg) and concentrated hydrochloric acid (5 cm³) were mixed at −78 °C, then warmed to room temperature and kept at this temperature for 3 h. The evolved gases were trapped at −190 °C, analyzed by g.l.c., and shown in all cases to be a mixture of n-butane and n-butenes. In the cases of (1) and (4) a microcrystalline solid was formed during the reaction, which was separated and washed thoroughly with water and diethyl ether and identified as [$PdCl_2$(dppe)] [13] and [$PdCl_2(PPh_3)_2$],[16] respectively. In the cases of (2) and (3) metallic palladium precipitated.

With bromine. In a typical experiment, to a solution of the metallacycle (0.2 mmol) in CH_2Cl_2 (5 cm³), at −78 °C, was added bromine (0.45 mmol). The mixture was warmed to room temperature and stirred for 30 min. A solid which formed during the reaction was filtered off. The solution was extracted with water, then with a 10% aqueous solution of $Na_2[S_2O_3]$, and finally with water. The organic layer was found by g.l.c. to contain 1,4-dibromobutane as the only reaction product. The solid was purified and identified as [$PdBr_2$(dppe)] [17] in the case of (1), [$PdBr_2$(tmen)] [14] in the case of (2), and [$PdBr_2(PPh_3)_2$] [16] in the case of (4).

With CO. In a typical experiment a flask containing the metallacycle (50 mg) dissolved in toluene (5 cm³) at −50 °C was filled with CO at atmospheric pressure. The reaction mixture was stirred at this temperature for 1 h, then warmed to room temperature, and stirred for another 4 h. The volatile materials were distilled off *in vacuo* and trapped at −78 °C. G.l.c. analysis revealed the presence of cyclopentanone in the case of compounds (2)—(4) in addition to an unidentified product at higher retention times.

Reaction of (1) *with Sulphur Dioxide: Formation of* [1,2-*Bis*(*diphenylphosphino*)*ethane*](*butane*-1,4-*disulphinato*-SS′)*palladium*(II)–*Dichloromethane*(2/1), (5).—Compound (1) (96 mg, 0.17 mmol) was placed in a flask maintained at −40 °C. Dry SO_2 was then passed into the flask, where it condensed and dissolved the crystals of (1) to produce a red solution. As soon as all of the solid had dissolved, the addition of SO_2 was stopped and the solution kept at −40 °C for 3 h. The liquid was then removed by allowing the cold trap to warm to room temperature. The residue was then dissolved in CH_2Cl_2, and pentane added slowly with stirring to give yellow crystals, yield 100 mg (85%), m.p. (decomp.) 178 °C.

Reaction of [$PdMe_2$(dppe)] *with Sulphur Dioxide: Formation of* [1,2-*Bis*(*diphenylphosphino*)*ethane*]*bis*(*methanesulphinato*-S)*palladium*(II)–*Dichloromethane*(2/1), (6)—A similar reaction between [$PdMe_2$(dppe)] (120 mg, 0.224 mmol) and liquid SO_2 gave pale yellow crystals (from CH_2Cl_2–pentane), yield 116 mg (78%), m.p. (decomp.) 187—190 °C.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dibutylpalladium*(II), (7).—Butyl-lithium (2.38 cm³ of a 1.08 mol dm⁻³ diethyl ether solution, 2.58 mmol) was slowly added to a suspension of [$PdCl_2$(dppe)] (0.5 g, 0.86 mmol) in diethyl ether (30 cm³) at −70 °C. The suspension was stirred for 2 h, then warmed to room temperature, and stirred for another 3 h. The solid formed was separated from the solution, washed with diethyl ether, and extracted with toluene (30 cm³). The extracts were filtered and pentane was added to give cream crystals, yield 0.178 g (33%), m.p. (decomp.) 135—138 °C.

Reaction of (7) *with Sulphur Dioxide: Formation of* [1,2-*Bis*(*diphenylphosphino*)*ethane*]*bis*(*butanesulphinato*-S)-*palladium*(II)–*Dichloromethane*(1/1), (8).—Treatment of (7) (100 mg, 0.16 mmol) with SO_2 as described above gave yellow crystals (from CH_2Cl_2–pentane), yield 98 mg (82%), m.p. (decomp.) 180 °C.

Reaction of (1) *with* [CPh_3][BF_4]: *Formation of* [1,2-*bis*(*diphenylphosphino*)*ethane*](1—3-η-1-*methylallyl*)*palladium*(II) *Tetrafluoroborate*, (9).—Compound (1) (250 mg, 0.445 mmol) was dissolved in CH_2Cl_2 (5 cm³) and [CPh_3]-

$[BF_4]$ (176 mg, 0.445 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise with stirring. The resulting solution was added to a large excess of diethyl ether and a cream solid precipitated. The precipitate was filtered off and washed with diethyl ether, yield 240 mg (83%), m.p. (decomp.) 107—109 °C.

Reaction of (3) *with* $[CPh_3][BF_4]$: *Formation of* (2,2′-*Bipyridyl*)(1—3-η-1-*methylallyl*)*palladium*(II) *Tetrafluoroborate,* (10).—A similar reaction between (3) (90 mg, 0.28 mmol) and $[CPh_3][BF_4]$ (92 mg, 0.28 mmol) in CH_2Cl_2 gave orange crystals, yield 71 mg (62%).

Reaction of (4) *with* $[CPh_3][BF_4]$: *Formation of* (1—3-η-1-*Methylallyl*)*bis*(*triphenylphosphine*)*palladium*(II) *Tetrafluoroborate,* (11).—A similar reaction between (4) (250 mg, 0.364 mmol) and $[CPh_3][BF_4]$ (119 mg, 0.364 mmol) in CH_2Cl_2 gave yellow crystals, yield 197 mg (70%), m.p. (decomp.) 167—168 °C.

Reaction of (9) *with* LiMe.—Compound (9) (454 mg, 0.7 mmol) suspended in dry diethyl ether (25 cm^3) was treated with LiMe (1.4 mmol) giving a yellow solution. The mixture was cooled to 0 °C, water was added, and the mixture extracted with benzene. The solvent was removed and the solid residue crystallized from acetone. Crystals of $[PdMe_2(dppe)]$ separated (113 mg, yield 30%) (Found: C, 62.05; H, 5.00. Calc. for $C_{28}H_{30}P_2Pd$: C, 62.9; H, 5.65%); ^{1}H n.m.r. ($CDCl_3$), δ 0.43 (t, J = 7 Hz, Me), 2.21 [d, J(P–H) = 18 Hz, P–CH_2], and 7.3—7.8 p.p.m. (m, Ph).

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