Bis(arylazo-oximato)palladium(II); Synthesis, Palladium–Nitrogen Bond Lability, and Redox Activity

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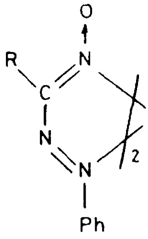
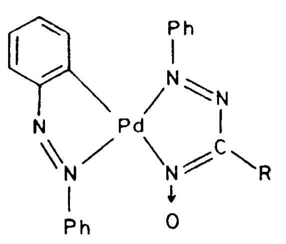
The synthesis and characterisation of the title complex, $[PdL_2]$ [L = PhN=NC(R)=NO], and related mixed-ligand complexes including [PdLA] (A = *ortho*-metallated azobenzene) are described. The mass spectrum of $[PdL_2]$ reveals peaks corresponding to loss of oximato-O and NO from the parent ion. Gaseous HCl cleaves the Pd–N-(oxime) bond selectively. Triphenylphosphine cleaves one or both Pd–N(azo) linkages giving $[PdL_2(PPh_3)]$ and unstable $[PdL_2(PPh_3)_2]$ which is also produced by oxidative addition of HL to $[Pd(PPh_3)_4]$. In $[PdL_2(PPh_3)]$ the unidentate and bidentate L groups scramble rapidly at 308 K but slowly at 233 K (^1H n.m.r.). Bidentate phosphine and phosphinoarsine cleave the two Pd–N(azo) bonds simultaneously. Unidentate amines, when present in very large excess, produce unstable $[PdL_2(amine)]$ in which one L is unidentate. Addition of X_2 (X = Cl or Br) yields the unstable palladium(IV) complex $[PdL_2X_2]$ which is readily reduced to halogeno-bridged palladium(II) species. A cyclic-voltammetric study of the one-electron quasi-reversible reduction of $[PdL_2]$, $[PdL_2(PPh_3)]$, [PdLA] *etc.* at a platinum electrode is briefly reported.

THE unique combination of oxime and azo-functions make arylazo-oximes excellent ligands for binding metal ions. The complexes display interesting stereochemical and reactivity patterns.[1] The palladium di-μ-halogeno-species, $[Pd_2X_2L_2]$ [L = PhN=NC(R)=NO; X = Cl or Br] were reported recently.[2,3] The synthesis, characterisation, and reactivity of the bis complex (1) form the primary subject matter of this report. One example of the related species (2) is also described.



(1)



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RESULTS AND DISCUSSION

Synthetic Reactions.—The compound HL reacts with PdX_4^{2-}, $[PdX_2(NCPh)_2]$, $[Pd_2X_2L_2]$, or bis(salicylaldehydato)palladium(II) to yield dark coloured crystals of $[PdL_2]$ which dissolve in organic solvents giving deep green solutions. With the first two starting materials, the formation of $[Pd_2X_2L_2]$ as an intermediate can be demonstrated. The azo-oxime ligand is believed to split the halogeno-bridge in this intermediate by the oxime-N end with concomitant elimination of HCl and closure of the second chelate ring. This sequence helps to rationalise the mixed-chelate forming reaction (1)

$$[Pd_2X_2L^1_2] + 2HL^2 \longrightarrow 2[PdL^1L^2] + 2HX \qquad (1)$$

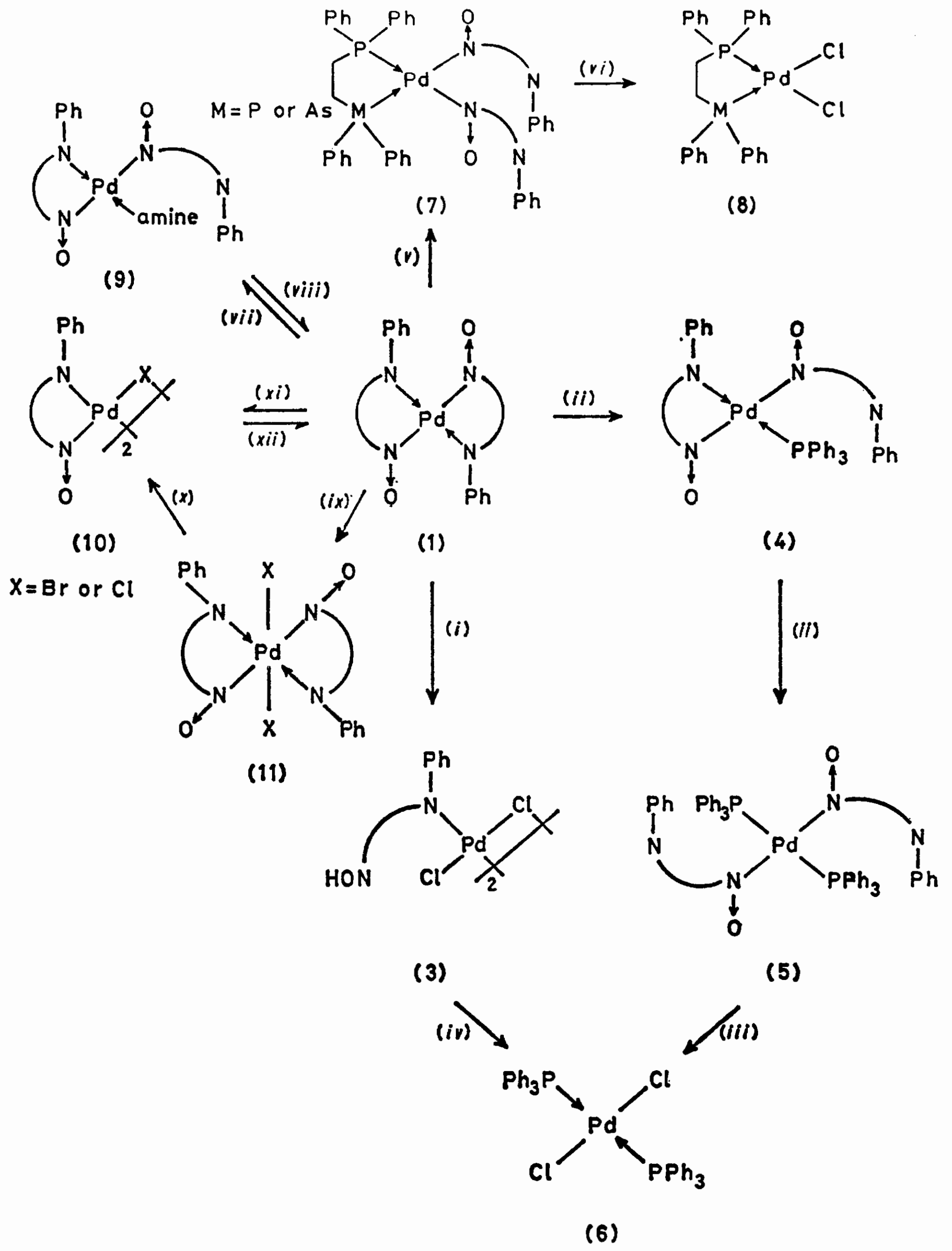
where L^1 = L with R = Me, and L^2 = L with R = Ph. This reaction is readily extended to prepare maroon crystals of $[PdL^2A]$ (2) by reacting the di-μ-chloro-complex[4] $[Pd_2Cl_2A_2]$ (A = *ortho*-metallated azobenzene) with HL^2. Reactions of (1) are summarized in the Scheme and characteristics of crystalline complexes are collected in Table 1. Unless otherwise stated in the text, the reactions in the Scheme refer to the complexes of ligand L^1.

Spectral Properties.—Only $[PdL^1_2]$ was volatile enough to give a satisfactory mass spectrum. Many metal-containing species could be identified using the isotopic abundance pattern. Apart from the molecular-ion peak at m/e = 430 (based on the ^{106}Pd isotope) significant peaks occur at m/e = 415, 414, 400, and 268 corresponding to loss of CH_3, O, NO, and L^1 respectively. The loss of oximato-O and NO from the parent ion is a characteristic feature of oxime complexes.[5]

A strong i.r. vibration in the 1 200—1 300 cm^{-1} region is due to ν(NO). In $[PdL^1L^2]$ two overlapping but distinct ν(NO) bands characterise the two chelate rings. The intense electronic transition at *ca.* 600 nm in $[PdL_2]$ is assigned to $d(Pd)\rightarrow\pi^*$ (chelated azo-oxime). In all complexes having only one chelated L per palladium, this band [2] is at *ca.* 500 nm. The considerable red shift observed for $[PdL_2]$ suggests the presence of metal-mediated interchelate delocalisation.

Ring-opening at the Oxime End.—Hydrogen chloride converts (1) to (3). Protonation of the oximato-function, cleavage of the Pd–N(oxime) bond by Cl^-, and finally dimerisation with partial ligand elimination is the probable reaction sequence. Significantly, hydrogen chloride is known to convert [2] (10) to (3). Other examples of the cleavage of the Pd–N(oxime) bond by hydrogen chloride are (5) ⟶ (6) and (7) ⟶ (8).

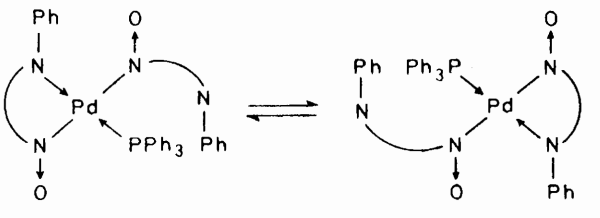
Dynamic Opening of One Chelate Ring.—Phosphines are known [2] to open the arylazo-oxime chelate rings selectively at the azo-end. One mole of PR'_3 (R′ = Ph, *m*-tolyl, or *p*-tolyl) converts green (1) to violet (4) having only one chelated L moiety (characteristic absorption at *ca.* 500 nm). Oxime-bound unidentate L^1 has a strong vibration at 1 430 cm^{-1} which is absent in chelated L^1. Complex (4) has this band. Sterically hindered phosphines like $P(o\text{-tolyl})_3$ and $P(cyclohexyl)_3$ fail to react with (1) and so does $AsPh_3$ (weak base).



SCHEME (*i*) HCl gas, C_6H_6, 298 K, hexane added; (*ii*) PPh_3, C_6H_6, 298 K; (*iii*) HCl gas, C_6H_6, 298 K; (*iv*) 4 PPh_3, C_6H_6, 298 K; (*v*) dppe or dadpe, C_6H_6, 298 K, 15 min stirring; (*vi*) HCl gas, $CHCl_3$, 298 K; (*vii*) amine (pyridine, aniline, γ-picoline), 298 K; (*viii*) dilution with C_6H_6; (*ix*) X_2 (X = Cl or Br), C_6H_6 or $CHCl_3$, 298 K; (*x*) evaporated, and ethanol added; (*xi*) (*a*) $[Pd(NCPh)_2Cl_2]\cdot C_6H_6$ or ethanol, 298 K; (*b*) PdX_2, ethanol, boil; (*xii*) 2HL, C_6H_6 and water, 15 min stirring, 298 K

Addition of PR'_3 to species in which the Pd–N(oxime) bond is already cleaved, leads to elimination of the L fragment, *e.g.* (3) ⟶ (6).

The value of δ(Me) (^1H n.m.r. in $CDCl_3$) for $[PdL^1_2]$ is 2.13 p.p.m. At room temperature complex (4) also has a single sharp Me signal but with δ = 1.82 p.p.m. Rapid scrambling of the chelated and unidentate ligands is implicated as shown in equilibrium (2). On cooling below 293 K, the Me signal broadens progressively and around 253 K splitting into two signals occurs. These sharpen on further cooling and finally at 233 K two well defined sharp signals of equal intensity remain (δ 2.16


(2)

and 1.44 p.p.m.) confirming that the instantaneous structure is indeed (4). The signal at higher field is assigned to unidentate L^1 since opening of the L^1 chelate ring by PPh_3 is known [2] to result in a considerable decrease in δ(Me). A probable mechanism for the fluxional behaviour would be intramolecular nucleophilic attack (S_Ni) by the pendant azo-group resulting in displacement of the bound azo-function. An example of the S_Ni path is documented [6] in the displacement of phosphine by a free azo-group [equilibrium (3)]. Process

$$[PdClA(PMePh_2)_2] \rightleftharpoons [PdClA(PMePh_2)] + PMePh_2 \quad (3)$$

(2) is unique in that both the forward and backward reactions must have identical S_Ni dynamics since the attacking and leaving groups are identical.

Opening of Both Rings.—The electronic spectrum of (4) in solution is not affected by the addition of one (or more) moles of PPh_3. However, on concentrating the solution, orange crystals (band at 465 nm) are deposited. When redissolved the transformation (5) ⟶ (4) + PPh_3 occurs spontaneously. In contrast, the yellow complex (7) having chelated 1,2-bis(diphenylphosphino)ethane (dppe) or 1-diphenylarsino-2-diphenylphosphinoethane (dadpe) is perfectly stable.

TABLE 1

Microanalytical and spectroscopic data for the palladium(II) complexes

	Compound	Analysis (%) [a] C	H	N	Pd	I.r.[b] ν(N–O)	^{1}H n.m.r.[c] δ(Me)	Electronic spectral data [d] λ(ε)
(1a)	$[PdL^1_2]$	44.2 (44.6)	3.8 (3.7)	19.1 (19.5)	24.8 (24.7)	1 280	2.13	625 (6 000), 585 (sh) (5 250)
(1b)	$[PdL^2_2]$	55.9 (56.2)	3.7 (3.6)	15.0 (15.1)	19.2 (19.3)	1 245		635 (6 000), 600 (sh) (5 350)
(1c)	$[PdL^3_2]$ [e]	58.1 (57.7)	4.1 (4.1)	14.3 (14.4)	18.4 (18.3)	1 245	[f]	645 (5 800), 605 (sh) (4 950)
(1d)	$[PdL^1L^2]$	51.9 (51.1)	3.9 (3.7)	17.1 (17.1)	21.1 (21.6)	1 265, 1 230	[f]	630 (5 000), 590 (sh) (4 200)
(2)	$[PdL^2A]$	58.2 (58.7)	3.8 (3.7)	13.5 (13.7)	20.2 (20.8)	1 240		570 (5 100)
(4)	$[PdL^1_2(PPh_3)]$	58.9 (58.9)	4.6 (4.5)	12.2 (12.1)	15.4 (15.4)	1 260	1.82 [g]	500 (7 000)
(5)	$[PdL^1_2(PPh_3)_2]$	65.1 (65.3)	4.9 (4.9)	8.7 (8.8)	11.2 (11.1)	1 250	1.82	465; [h] 500 (7 000)
(7a)	$[PdL^1_2(dppe)]$	60.2 (60.8)	4.8 (4.9)	10.3 (10.1)	12.8 (12.8)	1 250	1.80 [i]	415 (24 200), [j] 350 (36 500) [j]
(7b)	$[PdL^1_2(dadpe)]$	57.6 (57.7)	4.6 (4.6)	9.6 (9.6)	12.1 (12.2)	1 255		415 (15 040) [k]

[a] Calculated values are given in parentheses. [b] Values are in cm^{-1} (KBr disc); all ν(N–O) bands are very strong. [c] The values are in p.p.m. at 308 K unless otherwise noted; $CDCl_3$ and $SiMe_4$ were used as solvent and internal standard respectively; aromatic protons give signals in the region 6.7—9.0 p.p.m. and are not tabulated. [d] In benzene unless otherwise noted; λ = band maximum in nm; ε = absorption coefficient in $dm^3 mol^{-1} cm^{-1}$. [e] L^3 = L with R = *p*-tolyl. [f] Not soluble enough in the solvent stated. [g] At 233 K this signal is replaced by two signals of equal intensity at 1.44 and 2.16 p.p.m. [h] In the solid state. [i] Bridge methylene protons resonate at 2.1 and 2.3 p.p.m. [^2J(P–H) = 20 Hz]. [j] In chloroform. [k] A slight shoulder at *ca.* 500 nm may be due to partial opening of the dadpe chelate ring.

An alternative route to (5) is the oxidative addition of free ligand to $[Pd(PPh_3)_4]$, *e.g.* equation (4).

$$[Pd(PPh_3)_4] + 2HL^1 \longrightarrow [PdL^1_2(PPh_3)_2] + 2PPh_3 + H_2 \quad (4)$$

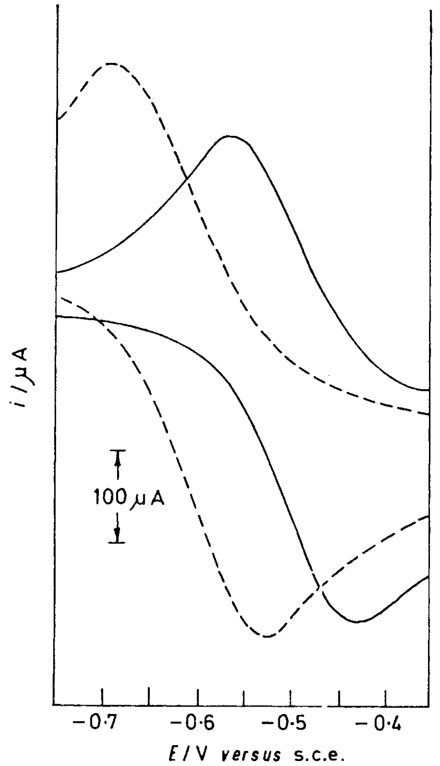
Reaction with Amines.—On passing ammonia gas into a green solution of $[PdL_2]$ the colour becomes red. The original colour is re-established on driving the ammonia out (by boiling or passing nitrogen through). The compound $[PdL_2]$ dissolves in neat aniline, pyridine, or γ-picoline to give red solutions. An intense band at 500 nm (ε for $[PdL^1_2]$: in aniline, 7 400; in pyridine, 7 000 $dm^3 mol^{-1} cm^{-1}$) characteristic of the solutions must be due to (9). On dilution with benzene, (1) is regenerated. Thus an amine can cleave one Pd–N(azo) bond when present in large excess. All attempts to isolate (9) in the crystalline state have failed. On concentration of the red solutions only $[PdL_2]$ crystallised out.

Oxidative Addition of X_2.—Solutions of $[PdL_2]$ in benzene on treatment with one equivalent of X_2 yield deep red solutions in which diamagnetic species with δ(Me) 2.33 (X = Cl) or 2.40 p.p.m. (X = Br) are present. The species (11) is believed to be present in solution. While the corresponding platinum(IV) complex is known [7] in the crystalline state, (11) is unstable as expected,[8] even in solution, and is readily reduced [2] to $[Pd_2X_2L_2]$.

Cyclic Voltammetry.—The compound $[PdL_2]$ undergoes a quasi-reversible one-electron reduction at a platinum electrode (Figure) around 0.5 V [reaction (5)].

$$[PdL_2] + e^- \longrightarrow [PdL_2]^- \quad (5)$$

The $[PdL_2]^-$ species contain palladium in the unusual [9] formal oxidation state +1. Species which have only one arylazo-oximato-chelate ring per palladium also show a similar couple but at relatively more negative potential (Table 2). A detailed account of the rich electrochemistry and related studies of palladium and platinum arylazo-oximates will be reported separately.



Cyclic voltammogram of $[PdL^2_2]$ (—) and $[PdL^2_2(PPh_3)]$ (- - -) in CH_2Cl_2–0.1 mol dm^{-3} $[NEt_4][ClO_4]$ (Pt electrode; scan rate, 50 mV s^{-1}; 298 K; solute concentration, *ca.* 10^{-3} mol dm^{-3})

EXPERIMENTAL

Chemicals and Starting Materials.—These were procured or synthesised as before.[2]

Measurements.—Infrared, electronic, and n.m.r. spectra were obtained as before.[2] Mass spectra were recorded on a Hitachi RMS-4 spectrometer operating at 80 eV * and by use of a direct insertion probe at *ca.* 493 K. Cyclic voltammetry was performed using a Princeton Applied Research 174A polarographic analyser, 175 universal programmer, and RE 0074 XY recorder. All operations were carried out under nitrogen in a three-electrode configuration. The working electrode was planar platinum of Beckman 39273 type.

TABLE 2

Cyclic voltammetric data[a] at 298 K (scan rate 50 mV s^{-1})

Compound	$-E_{pc}$	$-E_{pa}$	$-E_{298}^0$
		V	
$[PdL^1_2]$	0.56	0.49	0.53
$[PdL^2_2]$ [b]	0.57	0.43	0.50
$[PdL^1_2(PPh_3)]$	0.80	0.71	0.75
$[PdL^2_2(PPh_3)]$ [b,c]	0.69	0.53	0.61
$[PdL^2A]$	0.77	0.70	0.74
$[PdClL^2(PPh_3)]$ [d]	0.72	0.65	0.68
$[PdClL^2(py)]$ [e]	0.70	[f]	

[a] Unless otherwise noted solvent is acetonitrile; 0.1 mol dm^{-3} $[NEt_4][ClO_4]$. E_{pc} = Cathodic peak potential; E_{pa} = anodic peak potential; $E_{298}^0 = 0.5(E_{pa} + E_{pc})$, formal electrode potential. All potentials referred to saturated calomel electrode (s.c.e.) uncorrected for junction potential. [b] Solvent is CH_2Cl_2–0.1 mol dm^{-3} $[NEt_4][ClO_4]$. [c] Generated *in situ* in the electrochemical cell by adding PPh_3 to $[PdL^2_2]$; formation of complex confirmed by the appearance of a strong band at 525 nm. [d] Described in ref. 2. [e] Described in ref. 3 (py = pyridine). [f] Irreversible response, no anodic peak.

Syntheses of Compounds.—In general, compounds of the same type were prepared using similar methods. Details are given for a representative complex in each case.

*Bis(α-phenylazoacetaldoximato-*N,N''*)palladium*(II), (1a).—This was prepared by four different methods. (*a*) To a solution of $K_2[PdCl_4]$ (326 mg, 1 mmol) in water (30 cm^3) was added very slowly, dropwise with stirring, a solution of phenylazoacetaldoxime (570 mg, 3.5 mmol) in ethanol (15 cm^3). During the initial stage of ligand addition, a violet precipitate of $[Pd_2Cl_2L^1_2]$ formed, which slowly turned black as the addition was completed. The mixture was further stirred for 15 min. The precipitate was filtered off, washed thoroughly with water, dried, and was finally recrystallised from a benzene–hexane mixture (yield *ca.* 75%). (*b*) To a solution of $[Pd(NCPh)_2Cl_2]$ (384 mg, 1 mmol) in 95% ethanol (30 cm^3) was added slowly with stirring a solution of phenylazoacetaldoxime (326 mg, 2 mmol) in ethanol (15 cm^3). The subsequent procedure was the same as in (*a*) (yield *ca.* 70%). (*c*) A solution of di-μ-chloro-bis[(α-phenylazoacetaldoximato-*N,N''*)palladium(II)] (182 mg, 0.3 mmol) in benzene (30 cm^3) was mixed with a solution of phenylazoacetaldoxime (98 mg, 0.6 mmol) in benzene (10 cm^3) and the resulting brown solution was poured into water (25 cm^3) and stirred. The deep green benzene layer was separated from the aqueous layer and concentrated to *ca.* 5 cm^3. On adding hexane (10 cm^3), dark shining crystals separated. The crystals were filtered off, washed with hexane, and dried in air (yield *ca.* 75%). (*d*) Addition of phenylazoacetaldoxime (326 mg, 2 mmol) to a solution of bis(salicylaldehydato)palladium(II) (348 mg, 1 mmol) in benzene (20 cm^3) resulted in a deep green solution. After the solution had been concentrated to *ca.* 5 cm^3 addition of hexane (*ca.* 10 cm^3) deposited dark crystals.

(*α-Phenylazoacetaldoximato-*N,N'')(*α-phenylazobenzaldoximato-*N,N'')*palladium*(II), (1d).—A solution of di-μ-chloro-bis[(α-phenylazoacetaldoximato-*N,N''*)palladium(II)] (182 mg, 0.3 mmol) in benzene (30 cm^3) was mixed with a solution of phenylazobenzaldoxime (135 mg, 0.6 mmol) in benzene (10 cm^3) and the brown solution thus produced was treated in the same way as in method (*c*) for the synthesis of bis(α-phenylazoacetaldoximato-*N,N''*)palladium(II).

(*α-Phenylazobenzaldoximato-*N,N'')(*2-phenylazophenyl-*C^1,N')*palladium*(II), (2).—Di-μ-chloro-bis[(2-phenylazophenyl-*C*^{1},*N'*)palladium(II)] (258.4 mg, 0.4 mmol) was dissolved in benzene (50 cm^3) and to it a solution of phenylazobenzaldoxime (180 mg, 0.8 mmol) in benzene (10 cm^3) was added. The resulting brown solution was heated to boiling with anhydrous sodium carbonate (2 g) and stirred for 10 min. The violet solution was filtered and hexane was added to the filtrate. On scratching, red crystals separated out. These were filtered off and washed with hexane. Recrystallisation was carried out from a benzene–hexane mixture (yield *ca.* 60%).

Di-μ-*chloro-bis[chloro(α-phenylazoacetaldoxime-*N'')*palladium*(II)], (3).—Bis(α-phenylazoacetaldoximato-*N,N''*)palladium(II) (250 mg) was dissolved in benzene (20 cm^3) and a slow stream of dry HCl gas was passed through the solution. The solution turned orange-red and red crystals were deposited on adding hexane (*ca.* 10 cm^3). These were collected and characterised as described elsewhere.[2]

(*α-Phenylazoacetaldoximato-*N)(*α-phenylazoacetaldoximato-*N,N'')(*triphenylphosphine*)*palladium*(II), (4).—A solution containing bis(α-phenylazoacetaldoximato-*N,N''*)palladium-

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

(II) (215 mg, 0.5 mmol) and triphenylphosphine (131 mg, 0.5 mmol) in benzene (20 cm^3) was slowly evaporated to dryness under low pressure when a violet residue was left. The residue on recrystallisation from hexane yielded the pure crystalline product (yield *ca.* 70%).

Bis(α-*phenylazoacetaldoximato*-N)*bis*(*triphenylphosphine*)-*palladium*(II), (5).—This complex was made by two different methods. (*a*) A solution of triphenylphosphine (524 mg, 2 mmol) in benzene (15 cm^3) was mixed with a solution of bis(α-phenylazoacetaldoximato-*N,N''*)palladium(II) in benzene (15 cm^3). The resulting orange solution was allowed to evaporate slowly under reduced pressure. Orange crystals started separating out when the volume of the solution was *ca.* 5 cm^3. The crystals were filtered off and washed with the minimum volume of cold hexane and dried *in vacuo* (yield *ca.* 60%). (*b*) Tetrakis-(triphenylphosphine)palladium(0) was synthesised as described in the literature.[10] To a stirred suspension of tetrakis(triphenylphosphine)palladium(0) (231 mg, 0.2 mmol) in anhydrous ethanol (20 cm^3) under nitrogen was added a solution containing phenylazoacetaldoxime (66 mg, 0.4 mmol) in anhydrous ethanol (10 cm^3). Stirring was continued for 24 h and orange crystals of [PdL$^1_2$(PPh$_3$)$_2$] deposited. The crystals were filtered off, washed with anhydrous ethanol (all the operations were carried out in a nitrogen atmosphere), and dried *in vacuo* (yield *ca.* 75%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*bis*(α-*phenylazo-acetaldoximato*-N,)*palladium*(II), (7a).—To a solution of bis(α-phenylazoacetaldoximato-*N,N''*)palladium(II) (215 mg, 0.5 mmol) in benzene (20 cm^3) was added with stirring a solution of 1,2-bis(diphenylphosphino)ethane (200 mg, 0.5 mmol) in benzene (10 cm^3). The initial green colour changed to orange and as the stirring was continued the required complex separated as an orange solid which was filtered off, washed with benzene, and recrystallised from chloroform (yield *ca.* 65%).

(1-*Diphenylarsino*-2-*diphenylphosphinoethane*)*bis*(α-*phenylazoacetaldoximato*-N)*palladium*(II), (7b).—A solution containing 1-diphenylarsino-2-diphenylphosphinoethane (dadpe) (221 mg, 0.5 mmol) in benzene (10 cm^3) was added to a solution of bis(α-phenylazoacetaldoximato-*N,N''*)palladium(II) (215 mg, 0.5 mmol) in benzene (20 cm^3). The resulting deep red solution was slowly concentrated to *ca.* 5 cm^3. Orange needles of [PdL$^1_2$(dadpe)] were deposited. The crystals were filtered off, washed with the minimum volume of cold benzene, and dried *in vacuo* (yield *ca.* 60%).

Reaction of Gaseous HCl *with* [1,2-*Bis*(*diphenylphosphino*)-*ethane*]*bis*(α-*phenylazoacetaldoximato*-N,)*palladium*(II), (7a).—The complex (82 mg, 0.1 mmol) was dissolved in chloroform (20 cm^3) and a slow stream of HCl gas was passed through it. The passage of the gas was stopped when the orange colour of the solution changed to yellow. On concentrating the yellow solution to *ca.* 2 cm^3, [PdCl$_2$-(dppe)] crystallised out (yield *ca.* 85%).

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