Selective Cleavage of the Two Types of Pd–N Bonds in Di-μ-halogeno-bis[arylazo-oximatopalladium(II)]

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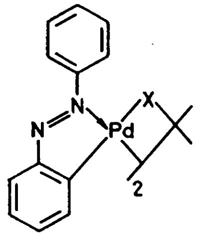
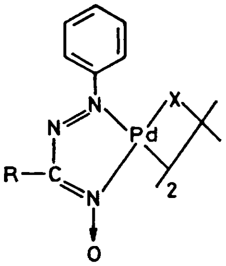
Triarylphosphines split the halogen bridge of the title complex and also open the arylazo-oximato chelate ring at the azo-end. In solution an equilibrium exists between the closed-ring and open-ring species. The equilibrium constants are reported. Bidentate phosphine and phosphinoarsine simultaneously split the bridge and cleave the Pd–N(azo) bond. Anhydrous HCl gas protonates the oximato-group with its concomitant displacement by Cl^- ion; in effect the Pd–N(oxime) bond is selectively cleaved.

UNLIKE azobenzene [1] which undergoes palladation to (1), phenylazoaldoximes yield (2) due to rapid chelation [2] of the palladium centre by the deprotonated oxime function. The complex (2), like (1), [3-6] is shown to undergo splitting of the Pd_2X_2 bridge by phosphorus donors. The major emphasis in the present study, however, pertains to cleavage of the Pd–N(azo) and Pd–N(oxime) bonds and to the equilibria associated with the Pd–N(azo) cleavage.



(1)



(2)

RESULTS AND DISCUSSION

The reported synthetic method [2] to give (2) often yields a product contaminated by the bis complex $[PdL_2]$ [L = organic ligand in (2)]. It is now shown that dissolved $[Pd(NCPh)_2X_2]$ or suspended PdX_2 (X = Cl or Br) reacts with ethanolic phenylazoaldoxime to produce (2) in a pure state. Oxidation of $[PdL_2]$ by X_2 followed by reduction with hot ethanol also gives rise to (2) in good yield; the intermediate is believed to be a palladium(IV) species. The expected [3] bridge Pd–X stretches are present in (2). The various reactions of (2) are summarised in the Scheme and characteristics of various products are collected in the Table.

Reactions with MR'_3 (M = P *or* As).—Triphenylarsine and the following phosphines have been used: R′ = Ph, *o*-tolyl, *m*-tolyl, and *p*-tolyl. Violet crystals of $[PdXL(MR'_3)]$ (3) result from bridge-splitting reactions and from redistribution reaction between $[PdL_2]$ and *trans*-$[PdX_2(MR'_3)_2]$. Triarylphosphines quantitatively displace amine from [PdXL(amine)] [7] producing $[PdXL(PR'_3)]$.

One characteristic feature of (3) (Table) is an allowed $d(Pd)\rightarrow\pi^*$ (chelated azoimine) [8] electronic transition at *ca.* 520 nm which is common to all complexes {(2), (3), (9), and [PdXL(amine)] [7]} containing the chelated moiety PdL. When the chelate ring, L, is opened at either end, the band at *ca.* 520 nm disappears.

Bright orange crystals of (4) have an electronic band at 465 nm. The absence of a band at *ca.* 520 nm excludes structures with chelated L such as $[PdL(PR'_3)_2]Cl$ and $[PdClL(PR'_3)_2]$. The 1 : 1 electrolytic formulation is further disproved by electrical conductivity data and by the presence of ν(Pd–Cl). In (4) a new vibration of medium intensity arises around 1 490 cm^{-1}. In (3) and in a variety of arylazo-oximates with chelated L^1 (L^1 = L with R = Me), δ(Me) is *ca.* 2 p.p.m.[2,7] In (4) δ(Me) is 0.87 p.p.m., possibly due to orientation of the methyl group well into the shielding cones of the phenyl rings of PPh_3. Behaviour of this kind is known [9] but in no case is the effect so dramatic.

Concentrated solutions of (4) (R = Me, R′ = Ph, X = Cl or Br) in organic solvents are orange in colour. On dilution, the colour becomes red and bands at 515, 430, and 330 nm appear (benzene solution). The intensity of the band at 515 nm which is indicative of the presence of (3) increases with dilution and the spectrum finally approaches that of pure (3). Addition of PPh_3 brings about a reverse effect. The equilibrium (1) is present.

$$(3;\ R = Me,\ X = Cl\ or\ Br) + PR'_3 \rightleftharpoons (4) \qquad (1)$$

The equilibrium constants (*K*) for reaction (1) (X = Cl) in benzene were determined using the intensity of the band at *ca.* 520 nm as a measure of the concentration of (3). The values of the constant (298 K) are: PPh_3, 2.8×10^3; $P(p\text{-tolyl})_3$, 7.1×10^3; $P(m\text{-tolyl})_3$, 12.4×10^3 $dm^3\ mol^{-1}$. Unlike *K*, the proton affinities [10] of PR'_3 (*o*-tolyl < Ph < *p*-tolyl ∼ *m*-tolyl)/ do not discriminate between *para* and *meta* methyl substitution. Tri-*o*-tolylphosphine fails to open the chelate ring, L, evidently due to steric hindrance.

Reactions with Bidentate Phosphine and Phosphinoarsine.—The ligand 1,2-bis(diphenylphosphino)ethane (dppe) brings about simultaneous bridge-splitting and ring-opening reactions producing (6) (M = P), which is the sole species present both in the solid state and in solution.

The stability of the dppe chelate ring is thus higher than that of the L chelate ring. Also the facility of phosphine dissociation and ring closure in the process (4)→(3) is likely to be augmented by the mutual *trans*-labilising effect of the two PPh_3 ligands in (4). This does not apply to (6) which has two *cis* phosphorus atoms. The Pd–Cl stretch in (6) (X = Cl) appears at a lower energy than that in (4). In the former, the chloro-group is *trans* to a strongly labilising phosphorus atom while in the latter it is *trans* to the oximato-group of the L fragment.

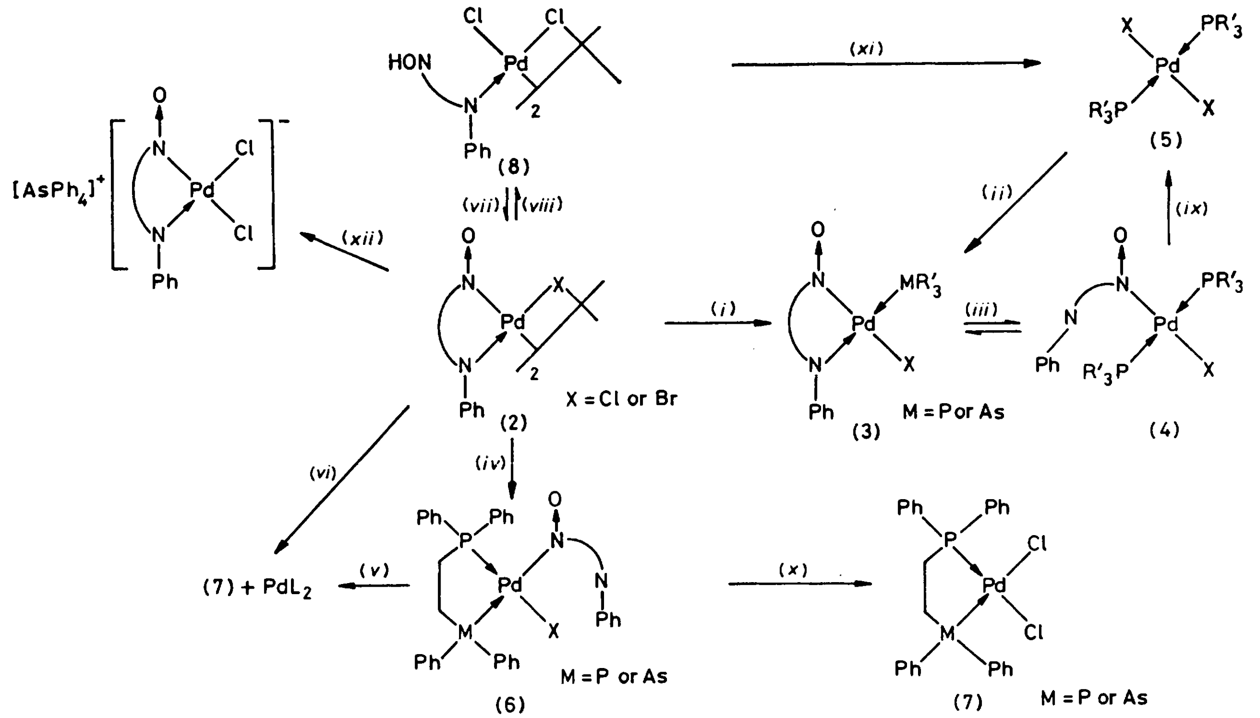
While $AsPh_3$ fails to open the azo-end of (3), the stability of the 1-diphenylarsino-2-diphenylphosphinoethane (dadpe) chelate ring augments the co-ordinating ability of the arsenic atom which is now able to cleave the Pd–N(azo) bond. The chloro-group in (6) (M = As) is *trans* to the phosphorus atom since ν(Pd–Cl) is at the same frequency as that of (6) (M = P). The Pd–Cl frequencies in *cis*-$[PdCl_2(MMe_3)_2]$ are known to vary considerably when M is changed from P to As.[11]

The 1 : 1 reaction between (2) (R = Me) and dppe (or dadpe) gives an equimolecular mixture of $[PdL^1_2]$ and (7). Further (2) (R = Me) reacts with two moles of (6) producing the same equimolecular mixture. Bridge splitting of (2) by the free azo-end of (6) followed by rearrangement of the resultant dinuclear intermediate with a bridging L, [LXPd(μ-L)PdXL], provides a possible rationale for these reactions.

Reaction with Hydrogen Chloride.—The neutral oxime function is a weaker donor than the oximato-anion. Hydrogen chloride protonates the oximato-function of (2) and the resultant chloride ion brings about the displacement Pd–N(oxime)→Pd–Cl thus opening the chelate ring selectively at the oxime end. Red crystals of (8), however, readily lose hydrogen chloride to regenerate (2) particularly in the presence of bases including moisture. By careful manipulation the i.r. spectra of (8) could be recorded. Specific ν(O–H) (broad and strong) and ν(Pd–Cl) (strong and sharp) frequencies are respectively: $[Pd_2L^2_2Cl_4]$, 3 140, 350; $[Pd_2L^3_2Cl_4]$, 3 100, 355; $[Pd_2L^4_2Cl_4]$, 3 020, 355 cm^{-1} (L^2,L^3,L^4 represent phenylazoaldoxime where R = Me, Ph, and *p*-tolyl respectively). The electronic spectra of (8) in benzene (saturated with HCl gas) exhibit an intense band at *ca.* 400 nm, *e.g.* R = Me, 385 nm (19 500 cm^{-1}).

When chloride ions are used but protons are not supplied, the chelate ring, L, remains intact and (2) is converted to the relatively uncommon[12] anionic *cis* dichloro-species (9) which is a 1 : 1 electrolyte in nitromethane solution (Λ_M = 120 S cm^2 mol^{-1} at 303 K).

Addition of PPh_3 to (8) frees the palladium atom from bound arylazo-oxime: (8)→(5). When HCl gas reacts with (4), (5) is formed. Thus starting from (2), the L fragment can be removed *via* (4) or *via* (8). Similar ligand elimination reactions are also observed with (6).



SCHEME (*i*) $2PR'_3$ or $2AsPh_3$, CH_2Cl_2 or C_6H_6, 298 K, 10 min stirring; (*ii*) PdL_2 (R = Me), $CHCl_3$ or C_6H_6, 298 K, 10 min stirring; (*iii*) PR'_3, C_6H_6, 298 K; (*iv*) 2 dppe or 2 dadpe, C_6H_6, 298 K, 15 min stirring; (*v*) 0.5 $[\{PdClL'\}_2]$, C_6H_6, 298 K, 15 min stirring; (*vi*) dppe or dadpe, C_6H_6, 298 K, 10 min stirring; (*vii*) X = Cl, C_6H_6, HCl gas, 298 K, hexane added; (*viii*) moist air (or pour into H_2O), 298 K, 10 min; (*ix*) X = Cl, C_6H_6, HCl gas, 298 K; (*x*) X = Cl, $CHCl_3$, HCl gas, 298 K; (*xi*) C_6H_6, PPh_3, 298 K; (*xii*) $2[AsPh_4]Cl$, X = Cl, CH_2Cl_2, 298 K, 15 min stirring

EXPERIMENTAL

Chemicals and Starting Materials.—The palladium-containing starting materials were obtained commercially or were prepared as described in the literature. Arylazo-oximes were synthesised following the procedure of Bamberger and Pemsel with some modifications.[2] Tetraphenylarsonium chloride, the phosphines, and the arsines were procured either from Aldrich Chemical Co. (U.S.A.) or from Strem Chemicals Inc. (U.S.A.).

Measurements.—Infrared spectra were recorded on either a Perkin-Elmer 521 or a Beckman IR-20A spectrophotometer (KBr discs); Hydrogen-1 n.m.r. spectra were obtained with either a Varian T-60A or a Varian EM-390 spectrometer ($CDCl_3$ solutions); the electronic spectra were measured with a Cary 14 recording spectrophotometer.

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.

Microanalytical and spectroscopic data for the palladium(II) complexes

		Analysis (%) [a]				I.r. data [b]			^{1}H n.m.r. [c]	Electronic [d] spectral data
	Compound	C	H	N	Pd	ν(N–O)	ν(Pd–Cl$_t$)	ν(Pd–Cl$_b$)	δ(Me)	$\lambda(\varepsilon)$
(2a)	$[\{PdClL^1\}_2]$	31.5 (31.6)	2.7 (2.6)	13.7 (13.8)	34.9 (35.0)	1 275vs 1 230		325m 295m	*e*	535 (5 100)
(2b)	$[\{PdBrL^1\}_2]$	28.1 (27.6)	2.3 (2.3)	12.0 (12.0)	30.5 (30.5)	1 270vs 1 215s		218m	*e*	545 (5 300)
(2c)	$[\{PdClL^5\}_2]$	42.8 (42.6)	2.7 (2.7)	11.5 (11.5)	29.1 (29.0)	1 230vs		294s 266m	*e*	*e*
(2d)	$[\{PdBrL^5\}_2]$	38.1 (38.0)	2.5 (2.5)	10.3 (10.2)	26.10 (25.9)	1 230vs		168s	*e*	*e*
(2e)	$[\{PdClL^6\}_2]$	44.3 (44.2)	3.2 (3.2)	11.1 (11.0)	28.1 (28.0)	1 230s			*e*	*c*
(2f)	$[\{PdBrL^6\}_2]$	39.5 (39.6)	2.8 (2.8)	10.0 (9.9)	25.1 (25.0)	1 230s			*e*	*e*
(3a)	$[PdClL^1(PPh_3)]$	55.4 (55.2)	3.9 (4.1)	7.5 (7.4)	19.3 (19.5)	1 270vs	350s		2.03 (br)	515 (5 200)
(3b)	$[PdBrL^1(PPh_3)]$	51.3 (51.1)	3.8 (3.8)	6.8 (6.8)	17.4 (17.4)	1 270vs			2.13	520 (5 400)
(3c)	$[PdClL^1\{P(p\text{-tolyl})_3\}]$	57.3 (57.2)	4.7 (4.8)	7.0 (6.9)	17.6 (17.5)	1 260vs	355m		2.10 [f]	515 (6 500)
(3d)	$[PdBrL^1\{P(p\text{-tolyl})_3\}]$	53.2 (53.3)	4.5 (4.5)	6.4 (6.4)	16.3 (16.3)	1 265vs			2.13 [f]	520 (6 400)
(3e)	$[PdClL^6(PPh_3)]$	59.8 (59.8)	3.9 (4.0)	6.5 (6.5)	16.5 (16.6)	1 245s	350m		*g*	540 (5 700)
(3f)	$[PdBrL^6(PPh_3)]$	55.7 (55.9)	3.8 (3.8)	6.1 (6.1)	15.4 (15.5)	1 240vs			*h*	540 (5 850)
(3g)	$[PdClL^1(AsPh_3)]$	51.3 (51.2)	3.7 (3.8)	6.7 (6.9)	17.5 (17.4)	1 270s	345m		2.12 (br)	520 (5 400)
(3h)	$[PdBrL^1(AsPh_3)]$	47.5 (47.7)	3.5 (3.5)	6.4 (6.4)	16.1 (16.3)	1 265vs			2.13	520 (5 500)
(4a)	$[PdClL^1(PPh_3)]$	63.4 (63.7)	4.5 (4.6)	5.2 (5.0)	12.7 (12.8)	1 265vs	335m		0.87	*i*
(4b)	$[PdBrL^1(PPh_3)]$	60.5 (60.5)	4.4 (4.4)	4.8 (4.8)	12.3 (12.2)	1 255s			0.87	*i*
(6a)	$[PdClL^1(dppe)]$	58.0 (58.1)	4.6 (4.6)	5.9 (6.0)	15.2 (15.1)	1 250vs	312m		1.80 [j]	*k*
(6b)	$[PdBrL^1(dppe)]$	54.5 (54.6)	4.3 (4.3)	5.7 (5.6)	14.1 (14.2)	1 250vs			1.80 [l]	*m*
(6c)	$[PdClL^5(dppe)]$	61.3 (61.2)	4.5 (4.5)	5.5 (5.5)	14.1 (13.9)	1 260s			*e*	*e*
(6d)	$[PdClL^1(dadpe)]$	54.6 (54.7)	4.3 (4.3)	5.6 (5.6)	14.1 (14.3)	1 255vs	312m		*e*	*e*
(6e)	$[PdBrL^1(dadpe)]$	51.2 (51.6)	4.1 (4.1)	5.3 (5.3)	13.4 (13.5)	1 250s			*e*	*e*
(9)	$[AsPh_4][PdCl_2L^1]$	53.3 (53.1)	3.8 (3.9)	5.8 (5.8)	14.8 (14.7)	1 260s	330, 300		2.1	545 (5 600)

L^5 = L with R = Ph, L^6 = L with R = *p*-tolyl.

[a] Calculated values are given in parentheses. [b] The values are in cm^{-1}; in KBr disc; vs = very strong, s = strong, m = medium; Cl$_t$ = terminal chlorine, Cl$_b$ = bridging chlorine. [c] The values are in p.p.m.; $CDCl_3$ and $SiMe_4$ were used as the solvent and internal standard respectively; br = broad; aromatic protons give signals in the region 6.70—8.50 p.p.m. and are not tabulated. [d] In benzene; λ = band maximum in nm; ε = absorption coefficient per Pd atom in dm^3 mol^{-1} cm^{-1}; for the complexes $[PdClL^1(C_5H_5N)]$, $[PdBrL^1(C_6H_5NH_2)]$, and $[PdClL^6(\gamma\text{-picoline})]$ $\lambda(\varepsilon)$ values are 520 (5 350), 515 (5 800), and 555 (5 450) respectively. [e] Not soluble in the solvent stated. [f] δ(Me) (*p*-tolyl) = 2.33 p.p.m. [g] δ(Me) (*p*-tolyl) = 2.23 p.p.m. [h] δ(Me) (*p*-tolyl) = 2.27 p.p.m. [i] In benzene, the complex dissociates and an equilibrium is established (see text). [j] Bridge-methylene protons resonate at 2.33 and 2.53 p.p.m. ($^2J_{PH}$ = 20 Hz). [k] In $CHCl_3$, bands are at 410 nm (ε = 11 800), 340 nm (16 000), and 260 nm (28 000). [l] Bridge methylene protons resonate at 2.20 and 2.40 p.p.m. ($^2J_{PH}$ = 20 Hz). [m] In $CHCl_3$, bands are at 410 nm (ε = 12 100), 335 nm (16 500), and 260 nm (28 000).

Di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)].—This was prepared by three methods. (*a*). To a solution of $[Pd(NCPh)_2Cl_2]$ (384 mg, 1 mmol) in dehydrated ethanol (25 cm^3) was added with stirring a solution of phenylazoacetaldoxime (163 mg, 1 mmol) in dehydrated ethanol (15 cm^3). The mixture became violet coloured and violet crystals started depositing. After the addition of the ligand was complete, the mixture was stirred for 15 min. The crystals were then collected by filtration, washed with dehydrated ethanol, and dried over fused $CaCl_2$ (yield *ca.* 90%). Use of benzene in place of dehydrated ethanol as solvent produced similar results and yield.

(*b*). The compound $PdCl_2$ (177 mg, 1 mmol) was added to a solution of phenylazoacetaldoxime (163 mg, 1 mmol) in dehydrated ethanol (20 cm^3). The violet mixture was heated under reflux for 1 h and then cooled. The violet needle-shaped crystals were collected and treated as in (*a*) (yield *ca.* 85%).

(*c*). The green solution of bis(phenylazoacetaldoximato)-palladium(II) (250 mg) in benzene (15 cm^3) was carefully exposed to chlorine for *ca.* 10 s with constant stirring. The green colour rapidly changed to deep red. The exposure time was carefully controlled so that no precipitation occurred. The clear red solution was then slowly concentrated (on a hot plate) to 2 cm^3. Dehydrated ethanol (5 cm^3) was added when violet needles of the required complex were deposited. The crystals were collected and treated as in (*a*).

The corresponding bromo-bridged complexes were obtained from $[Pd(NCPh)_2Br_2]$ or $PdBr_2$ and arylazo-oximes following analogous procedures. The reaction of the bis(arylazo-oximate) species with bromine (molar ratio 1 : 1) in benzene also produced the bromo-bridged complexes.

Chloro(phenylazoacetaldoximato)(triphenylphosphine)palladium(II).—To a solution of di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)] (304 mg, 0.5 mmol) in dichloromethane (30 cm^3) was added with stirring a solution of triphenylphosphine (262 mg, 1 mmol) in dichloromethane (15 cm^3). The purple solution was then concentrated (on a hot plate) to *ca.* 2 cm^3 and hexane (5 cm^3) was added very slowly. The violet crystalline solid which deposited was filtered off, washed with hexane, and finally dried *in vacuo* (yield *ca.* 70%).

Reaction of Bis(phenylazoacetaldoximato)palladium(II) *with* trans-$[PdCl_2(PPh_3)_2]$.—A solution of bis(phenylazoacetaldoximato)palladium(II) (130 mg, 0.3 mmol) in benzene (20 cm^3) was slowly added with stirring to a solution of *trans*-bis(triphenylphosphine)palladium(II) chloride (210 mg, 0.3 mmol) in benzene (30 cm^3). After 15 min of stirring, the violet solution was slowly concentrated (on a hot plate) to *ca.* 2 cm^3 and hexane (5 cm^3) was added. The violet crystals of chloro(phenylazoacetaldoximato)(triphenylphosphine)palladium(II) which separated were filtered off, washed with hexane, and finally dried *in vacuo* (yield *ca.* 80%).

Reaction of Triphenylphosphine with Anilinechloro(phenylazoacetaldoximato)palladium(II).—A solution of triphenylphosphine (131 mg, 0.5 mmol) in benzene (10 cm^3) was added to a solution of anilinechloro(phenylazoacetaldoximato)palladium(II) (199 mg, 0.5 mmol) in benzene (15 cm^3) and the mixture was slowly concentrated (on a hot plate) to *ca.* 2 cm^3. On addition of hexane (5 cm^3), violet crystals of chloro(phenylazoacetaldoximato)(triphenylphosphine)-palladium(II) were deposited in *ca.* 80% yield.

Chloro(phenylazoacetaldoximato)bis(triphenylphosphine-palladium(II).—A mixture of di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)] (365 mg, 0.6 mmol) and triphenylphosphine (629 mg, 2.4 mmol) was dissolved in benzene (20 cm^3). The solution was then slowly concentrated *in vacuo* to *ca.* 2 cm^3. The deposited orange crystals were collected by filtration, washed with the minimum volume of cold hexane, and dried *in vacuo* (yield *ca.* 65%). The corresponding bromo-complex was synthesised similarly.

[1,2-*Bis(diphenylphosphino)ethane*]*chloro(phenylazoacetaldoximato)palladium*(II).—To a solution of di-μ-chloro-bis-[phenylazoacetaldoximatopalladium(II)] (122 mg, 0.2 mmol) in benzene (30 cm^3) was added with stirring a solution of 1,2-bis(diphenylphosphino)ethane (160 mg, 0.4 mmol) in benzene (5 cm^3). After 15 min of stirring the orange crystals were filtered off, washed with benzene, and dried *in vacuo* (yield *ca.* 80%).

Chloro(1-*diphenylarsino*)-2-*diphenylphosphinoethane-phenylazoacetaldoximatopalladium*(II) was prepared similarly by replacing 1,2-bis(diphenylphosphino)ethane with an equivalent amount (190 mg) of 1-diphenylarsino-2-diphenylphosphinoethane. The corresponding bromo-species was synthesised similarly.

Reaction of Di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)] *with* [1,2-*Bis(diphenylphosphino)ethane*]*chloro-(phenylazoacetaldoximato)palladium*(II).—To a solution of [1,2-bis(diphenylphosphino)ethane]chloro(phenylazoacetaldoximato)palladium(II) (141 mg, 0.2 mmol) in benzene (30 cm^3) was added with stirring a solution of di-μ-chloro-bis-[phenylazoacetaldoximatopalladium(II)] (61 mg, 0.1 mmol) in benzene (20 cm^3). After the precipitated $[PdCl_2(Ph_2PCH_2CH_2PPh_2)]$ was filtered off, the green filtrate was concentrated (on a hot plate) to *ca.* 5 cm^3 and hexane (5 cm^3) added to it when dark crystals of bis(phenylazoacetaldoximato)palladium(II) separated. The crystals were collected by filtration, washed with hexane, and dried in air.

1 : 1 *Reaction between Di-μ-chloro-bis[phenylazoacetaldoximatopalladium*(II)] *and* 1,2-*Bis(diphenylphosphino)ethane*.—A solution of 1,2-bis(diphenylphosphino)ethane (80 mg, 0.2 mmol) in benzene (5 cm^3) was added with stirring to a solution of di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)] (122 mg, 0.2 mmol) in benzene (25 cm^3). Precipitated $[PdCl_2(Ph_2PCH_2CH_2PPh_2)]$ was collected by filtration and crystals of bis(phenylazoacetaldoximato)-palladium(II) were obtained from the green filtrate.

Tetrachlorobis(phenylazoacetaldoxime)dipalladium(II).— A slow stream of HCl gas was passed through a solution of di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)] (*ca.* 50 mg) in benzene (*ca.* 20 cm^3). Addition of hexane (10 cm^3) to the orange-red solution precipitated red crystals of the complex.

Tetrachlorobis(phenylazobenzaldoxime)dipalladium(II).—Di-μ-chloro-bis[phenylazobenzaldoximatopalladium(II)] (*ca.* 30 mg) was suspended in benzene (20 cm^3) and through it a stream of HCl gas was passed while the whole mixture was stirred thoroughly. Slowly the purple solid turned red. The passage of HCl gas was continued until the entire solid (and the mother-liquor) was completely red.

Reaction of Gaseous HCl *with Chloro(phenylazoacetaldoximato)bis(triphenylphosphine)palladium*(II).—A slow stream of HCl gas was introduced into a solution of chloro-(phenylazoacetaldoximato)bis(triphenylphosphine)palladium(II) (*ca.* 100 mg) in benzene (15 cm^3). As a few bubbles of HCl were passed through the solution, light yellow crystals of *trans*-$[PdCl_2(PPh_3)_2]$ deposited. Free phenylazoacetaldoxime was isolated by evaporating the filtrate.

Reaction of Gaseous HCl with [1,2-*Bis(diphenylphosphino)ethane*]*chloro(phenylazoacetaldoximato)palladium*(II).—[1,2-Bis(diphenylphosphino)ethane]chloro(phenylazoacetaldoximato)palladium(II) (*ca.* 60 mg) was dissolved in chloroform (20 cm^3) and through it a slow stream of HCl gas was passed. 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, $[PdCl_2$-

$(Ph_2PCH_2CH_2PPh_2)]$ crystallised out. Free phenylazoacetaldoxime was obtained by evaporating the filtrate.

Reaction of Triphenylphosphine with Tetrachlorobis(phenylazoacetaldoxime)dipalladium(II).—Triphenylphosphine (*ca.* 250 mg) was added to a solution of tetrachlorobis(phenylazoacetaldoxime)dipalladium(II) (*ca.* 100 mg) {prepared *in situ* by passing HCl gas into the benzene solution of di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)]}. Pale yellow crystals of *trans*-$[PdCl_2(PPh_3)_2]$ were deposited on concentrating the light yellow solution to a small volume.

Tetraphenylarsonium Dichloro(phenylazoacetaldoximato)palladate(II).—A solution of tetraphenylarsonium chloride (252 mg, 0.6 mmol) in dichloromethane (10 cm^3) was added with stirring to a solution of di-μ-chloro-bis[phenylazoacetaldoximatopalladium(II)] (183 mg, 30 cm^3) in dichloromethane (30 cm^3). The solution was then completely evaporated in a rotary evaporator to a dark purple gum which was then dissolved in the minimum volume of hot benzene–hexane (1 : 1) mixture. Slow evaporation of the solution in air yielded purple crystals of the desired complex which were filtered off, washed with hexane, and finally dried in air (yield *ca.* 70%).

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