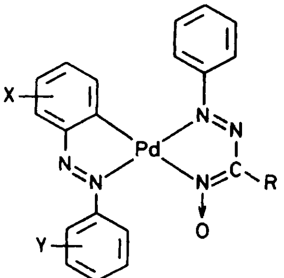
Arylazo-oximates of *ortho*-Palladated Azobenzenes: Synthesis, Isomerism, and Redox Behaviour

By **Pinaki Bandyopadhyay, Pradip K. Mascharak,** and **Animesh Chakravorty,*** Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

The synthesis and characterisation of new planar mixed species of the type [PdLA] (A = *ortho*-metallated azobenzene or its substituted derivative) is achieved by splitting the halogeno-bridge in $[Pd_2Cl_2A_2]$ by arylazo-oximes (HL). Triphenylphosphine cleaves the Pd-N(azo) bond in the PdL fragment, giving $[PdLA(PPh_3)]$. Many of the [PdLA] species occur as isomeric mixtures whose compositions have been established using ^1H n.m.r. data. The isomerism which originates from different modes of *ortho*-metallation of A is carried over to [PdLA] from the precursor complex $[Pd_2Cl_2A_2]$. A simple and accurate ^1H n.m.r. method of isomer analysis in $[Pd_2Cl_2A_2]$ is described. Substituent effects on isomer population are consistent with the electrophilic nature of the palladation reaction but steric effects also play dominant roles. The electrochemistry of [PdLA] has been thoroughly examined using cyclic voltammetry. Three couples are observed near -0.8, -1.2, and -1.5 V *vs.* standard calomel electrode, in acetonitrile. The first two couples correspond to successive one-electron reductions of the azo-functions of L and A respectively. The third couple is due to two-electron metal reduction.

AZOBENZENE becomes palladated [1-8] at the azo-nitrogen and *ortho*-carbon. Arylazo-oximes [9-11] bind palladium(II) through azo- and oximato-nitrogens. The chelate rings thus produced are five-membered and isoelectronic. In the present work the synthesis, structural characterisation, and ^1H n.m.r. assessment of isomer population of mixed chelates of type (1) are reported. The electrochemical redox activity of the azo-function in organic ligands and their metal complexes in aprotic solvents is potentially interesting but sparsely studied.[12-18] Complex (1) contains two types of chelated azo-groups and could thus display novel redox patterns. The electrochemistry of (1) was therefore investigated in some detail and the results are reported below.

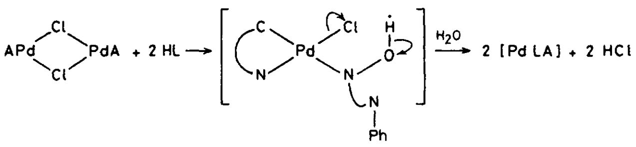


(1)

RESULTS AND DISCUSSION

Complex (1) is abbreviated as [PdLA] where L and A represent the arylazo-oxime and azobenzene moieties respectively. Specific abbreviations A^1—A^{19} for the ligand A depend on substituents and binding mode as set in Figure 1. In the case of L, the specific abbreviations are L^1 and L^2 for R = Me and Ph respectively. The complex $[PdL^2A^1]$ has been briefly reported earlier.[11] Physical data for the complexes, which are maroon to black, are collected in Table 1.

The complexes are synthesised by stoicheiometric cleavage of the halogeno-bridge in $[Pd_2Cl_2A_2]$ by HL (below). The reaction medium is a mixture of benzene and water; the presence of water, which acts as a base in the dehydrohalogenation reaction, is essential. The reaction can be rationalised *via* the intermediate as shown in the Scheme. In effect, the halogen bridge is split by the oxime-N atom with subsequent elimination of HCl and chelate ring closure. This proposal is based on two well documented facts: [10] the ready bridge-splitting in $[Pd_2Cl_2A_2]$ by Lewis bases and the facile dehydrohalogenation with attended chelate formation in complexes having an oxime group close to metal-bound halogen.



SCHEME

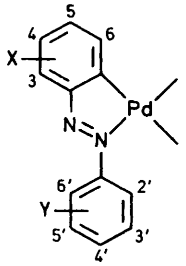


FIGURE 1 Isomeric modes of *ortho*-palladation of azobenzene

	X	Y		X	Y
A^1	H	H	A^{11}	6-Me	3′-Me
A^2	H	4′-Me	A^{12}	H	3′-OMe
A^3	5-Me	H	A^{13}	4-OMe	H
A^4	5-Me	4′-Me	A^{14}	6-OMe	H
A^5	H	4′-OMe	A^{15}	H	2′-Me
A^6	5-OMe	H	A^{16}	3-Me	H
A^7	H	3′-Me	A^{17}	3-Me	2′-Me
A^8	4-Me	H	A^{18}	H	2′-OMe
A^9	6-Me	H	A^{19}	3-OMe	H
A^{10}	4-Me	3′-Me			

All [PdLA] complexes display spectral characteristics of the PdL chelate ring: [10,11] a strong ν(NO) vibration in the range 1 150—1 250 cm^{-1} and an intense charge-transfer transition near 550 nm.

Isomerism.—For substituted azobenzenes, [PdLA] complexes often occur as a mixture of isomers (Table 1). However, in no case could the isomers be separated by chromatography on alumina or silica gel. In all such cases the characteristics (other than ^{1}H n.m.r.) of the crystalline complexes (Table 1) are those of isomeric mixtures. When A is symmetrical, no isomerism occurs proving that modes of binding of L are not responsible for isomerism in [PdLA] species. In fact the isomerism of (1) originates from that already existing in the precursor complex $[Pd_2Cl_2A_2]$. A simple and rapid ^{1}H n.m.r. method for assessment of isomer population in $[Pd_2Cl_2A_2]$ was therefore developed.

TABLE 1

Microanalytical, spectroscopic, and isomer population data for the palladium(II) complexes

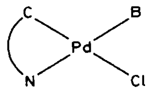
	Complex [a]	Analysis [b] (%) C	H	N	Pd	I.r.[c] ν(N–O)	^{1}H N.m.r.[d] Me (L^1)	Me (A)	Isomer population (%)	Electronic spectral data [e] λ (ϵ)
(1a)	$[PdL^1A^1]$	53.2	4.0	15.6	23.8	1 150	2.40			560
		(53.4)	(3.8)	(15.6)	(23.7)					(6 000)
(1b)	$[PdL^1A^2]$	54.6	4.0	15.3	22.9	1 155	2.40	2.23	43	555
	$[PdL^1A^3]$	(54.4)	(4.1)	(15.1)	(23.0)		2.40	2.53	57	(6 630)
(1c)	$[PdL^2A^2]$	58.9	3.8	13.2	20.0	1 245		2.23	42	570
	$[PdL^2A^3]$	(59.4)	(4.0)	(13.3)	(20.2)			2.50	58	(5 800)
(1d)	$[PdL^1A^4]$	55.6	4.2	14.7	22.0	1 155	2.4	2.23,		555
		(55.3)	(4.4)	(14.6)	(22.3)			2.50		(5 200)
(1e)	$[PdL^2A^4]$	59.5	4.0	12.8	19.2	1 240		2.23,		565
		(60.0)	(4.2)	(13.0)	(19.7)			2.50		(6 200)
(1f)	$[PdL^1A^5]$	52.0	4.1	14.2	22.0	1 160	2.46	3.70	40	555
	$[PdL^1A^6]$	(52.6)	(4.0)	(14.6)	(22.2)		2.46	4.10	60	(7 500)
(1g)	$[PdL^2A^5]$	57.5	3.8	12.7	19.2	1 235		3.70	40	570
	$[PdL^2A^6]$	(57.6)	(3.9)	(12.9)	(19.6)			4.06	60	(6 800)
(1h)	$[PdL^1A^7]$	54.2	4.0	15.0	22.8	1 150	2.40	2.40	35	575
	$[PdL^1A^8]$	(54.4)	(4.1)	(15.1)	(23.0)		2.40	2.10	65	(5 200)
(1i)	$[PdL^2A^7]$	59.1	4.1	13.1	20.0	1 235		2.40	35	565
	$[PdL^2A^8]$	(59.4)	(4.0)	(13.3)	(20.2)			2.10	65	(5 200)
(1j)	$[PdL^1A^{10}]$	55.0	4.3	16.8	22.1	1 150	2.43	2.43,		565
		(55.3)	(4.4)	(16.6)	(22.3)			2.06		(5 700)
(1k)	$[PdL^2A^{10}]$	59.7	4.0	13.2	20.0	1 240		2.40,		570
		(60.0)	(4.2)	(13.0)	(19.7)			2.06		(5 700)
(1l)	$[PdL^2A^{12}]$	57.5	4.0	12.7	19.9	1 230		3.80	30	580
	$[PdL^2A^{13}]$	(57.6)	(3.9)	(12.9)	(19.6)			3.60	70	(4 450),
										530
										(4 650)
(1m)	$[PdL^1A^{15}]$	54.8	4.2	15.4	23.3	1 145	2.43	2.71		565
		(54.4)	(4.1)	(15.1)	(23.0)					(5 200)
(1n)	$[PdL^2A^{17}]$	60.1	4.4	13.1	19.5	1 235		2.73,		565
		(60.0)	(4.2)	(13.0)	(19.7)			2.36		(5 000)
(1o)	$[PdL^1A^{18}]$	52.4	4.0	14.2	22.5	1 150	2.40	4.00		560
		(52.6)	(4.0)	(14.6)	(22.2)					(5 750)

[a] Compounds within a brace constitute an isomeric mixture. [b] Calculated values are in parentheses. [c] Values in cm^{-1} (KBr disc); all ν(N–O) bands are very strong. [d] Values are in p.p.m., $CDCl_3$ and $SiMe_4$ were used as solvent and internal standard respectively; aromatic proton signals are not tabulated. [e] Solvent was benzene; λ = band maximum (nm), ϵ = absorption coefficient (dm^3 mol^{-1} cm^{-1}).

Isomer estimation in $[Pd_2Cl_2A_2]$. The isomeric bonding modes concerned are given in Figure 1. Because of the insolubility of $[Pd_2Cl_2A_2]$ in common organic solvents direct isomer assessment by ^{1}H n.m.r. is not easily achieved.[5] Isomer assessment has been done *via* gas chromatographic analysis [3] of the products of exhaustive carbonylation of $[Pd_2Cl_2A_2]$. For fluoro-substituted azobenzenes,^{19}F n.m.r. has been applied after conversion of $[Pd_2Cl_2A_2]$ to soluble $[Pd(\eta\text{-}C_5H_5)A]$.[4] Our method is based on reaction (1) which solubilises $[Pd_2Cl_2A_2]$ instantly and completely in $CDCl_3$. The ^{1}H n.m.r. spectra of such solutions are utilised for isomer evaluation

$$[Pd_2Cl_2A_2] + 2\,B \longrightarrow 2[PdClAB] \qquad (1)$$
$$B = PPh_3,\ \text{aniline, or pyridine)}$$

(Table 2). The PPh_3 adducts usually provide the best information. From *X*-ray diffraction [6,7] and i.r.[8] data, it is known that in [PdClAB] the atomic arrangement is of type (2).



(2)

When B = PPh_3, positions 5- and particularly 6- of the metallated benzene ring come physically close to the phenyl groups of the PPh_3. The H^6 proton thus gets shielded and resonates at high field (δ 6.1—6.5 p.p.m.) well separated from other aromatic proton signals. When PPh_3 in (2) is replaced by aniline or pyridine, the H^6 signal shifts to lower field and becomes a part of the normal complex aromatic pattern.

In the case of methyl- or methoxy-substituted azobenzenes, consistent assignment of Me signals to isomers could be made from considerations of chemical shifts of free ligands and non-isomeric disubstituted symmetrical species (Table 2). Substituents on the non-metallated ring have chemical shifts very close to those of the corresponding free ligand. The 5-Me (5-OMe) signals appear at higher field compared to that of the 4-Me (4-OMe) signal. Replacement of PPh_3 by aniline or pyridine gives similar result but with smaller difference in chemical shifts. Isomers with 6-Me (6-OMe) (A^9, A^{11}, A^{14}) do not occur, evidently due to steric factors. The formation of the 3-Me (3-OMe) isomer (A^{16}, A^{19}) is at a statistical disadvantage with regard to that of the 2′-Me (2′-OMe) isomer (A^{15}, A^{18}). In practice, 3-Me (3-OMe) species are not observed at all. This is somewhat surprising since A^{17} exists.

TABLE 2

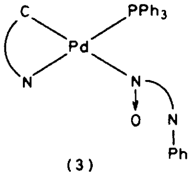
Hydrogen-1 n.m.r.[a] and isomer population data for [PdClAB] and $[PdL^1A(PPh_3)]$

Compound [b]	^1H N.m.r. δ Me (A)/ p.p.m.	Isomer population (%)
$\{[PdClA^2(PPh_3)]$	2.33	44}
$[PdClA^3(PPh_3)]$	1.80	56}
$\{[PdClA^2(an)]$	2.46	45}
$[PdClA^3(an)]$	2.30	55}
$[PdClA^4(PPh_3)]$	2.36, 1.77	
$[PdClA^4(an)]$	2.43, 2.30	
$\{[PdClA^5(PPh_3)]$	3.86	40}
$[PdClA^6(PPh_3)]$	3.13	60}
$\{[PdClA^5(py)]$	3.83	c }
$[PdClA^6(py)]$	3.80	}
$\{[PdClA^7(PPh_3)]$	2.40	36}
$[PdClA^8(PPh_3)]$	2.23	64}
$\{[PdClA^7(py)]$	2.36	35}
$[PdClA^8(py)]$	2.23	65}
$[PdClA^{10}(PPh_3)]$	2.40, 2.20	
$[PdClA^{10}(py)]$	2.36, 2.23	
$\{[PdClA^{12}(PPh_3)]$	3.83	20}
$[PdClA^{13}(PPh_3)]$	3.70	80}
$[PdClA^{15}(PPh_3)]$	2.71	
$[PdClA^{17}(PPh_3)]$	2.70, 2.53	
$[PdClA^{18}(PPh_3)]$	3.90	
$\{[PdL^1A^2(PPh_3)]$	2.23 [d]	42}
$[PdL^1A^3(PPh_3)]$	1.80 [d]	58}
$\{[PdL^1A^5(PPh_3)]$	3.73 [d]	40}
$[PdL^1A^6(PPh_3)]$	3.17 [d]	60}
$[PdL^1A^{15}(PPh_3)]$	2.73 [d]	
$[PdL^1A^{18}(PPh_3)]$	4.00 [d]	

[a] Values are in p.p.m., $CDCl_3$ and $SiMe_4$ were used as solvent and internal standard respectively; aromatic proton signals are not tabulated. [b] Compounds within a brace constitute an isomeric mixture; δ Me (OMe) chemical shifts of free substituted azobenzenes are: 4-Me (2.40), 4,4′-Me_2 (2.40), 4-OMe (3.76), 3-Me (2.40), 3,3′-Me_2 (2.33), 3-OMe (3.85), 2-Me (2.73), 2-OMe (3.86). an = Aniline, py = pyridine. [c] Integration was not possible due to overlapping signals. [d] Methyl protons of unidentate oxime-*N* bound arylazo-oxime (L^1) resonate at 1.33 p.p.m.

In cases where the metallation of both substituted (Me or OMe) and unsubstituted rings occurs, the population of the isomer having metallation in the substituted ring is higher, in line with the electrophilic nature of the palladation reaction. For example, the observed ratios of $[Pd_2Cl_2A^2{}_2]$: $[Pd_2Cl_2A^3{}_2]$ and $[Pd_2Cl_2A^5{}_2]$: $[Pd_2Cl_2A^6{}_2]$ are 7 : 9 and 2 : 3 respectively. These results are however in gross disagreement with those obtained by the carbonylation technique.[3] This technique is based on drastic chemical transformation. Our method is simple and direct, and the results are reproducible.

Isomer estimation in [PdLA]. The ^1H n.m.r. behaviours of corresponding L^1 and L^2 species are analogous except for the presence of an additional L^1 methyl signal at δ 2.4 p.p.m. The methyl resonances of A in isomeric species could be readily assigned to specific isomers (Table 1) by comparing them with signals of the corresponding free azobenzene and phosphine adduct (3) (Table 2). The population of isomers in various [PdLA] is entirely consistent with that of the precursor $[Pd_2Cl_2A_2]$.



(3)

The complex (3) is produced by adding triphenylphosphine to (1). In a chloroform solution of (3) [$L = L^1$] the L^1 methyl protons resonate at unusually high field. This characterises[10,11] a monodentate arylazo-oxime bound at the oxime-N atom only with the phosphine in a *cis* position as in (3). The methyl-H signals of the metallated ring in A and the H^6 proton signal in (3) [which merges with aromatic proton signals in the case of (1)] display high-field shifts as in (2) (Table 2)]. Complexes of type (3) have been isolated in the solid state in several cases and further details of their properties will be presented elsewhere.

Electrochemistry of [PdLA].—*Ligand reduction.* All complexes display (Figure 2) three cyclic voltammetric responses near −0.8, −1.2, and −1.5 V *vs.* s.c.e. (saturated calomel electrode) in acetonitrile solution at a platinum electrode and at a h.m.d.e. (hanging mercury drop electrode). The formal potential, $E_{298}{}^0$, for each couple was calculated as the average of cathodic and anodic peak potentials (Table 3). The couples near −0.8 and −1.2 are considered in this section. Voltammograms were recorded in the scan rate range v = 20—500 mV s^{-1}. The peak potentials are exactly or nearly invariant with v and the cathodic peak current (i_{pc}) is proportional to $v^{\frac{1}{2}}$. The peak-to-peak separation (ΔE_p) is in the range 60—80 mV. These facts taken in conjunction with current height and coulometric data settle the nearly or exactly reversible one-electron character of both couples. These can therefore be written as (2) and (3).

$$[Pd^{II}LA] + e^- \rightleftharpoons [Pd^{II}LA]^- \qquad (2)$$

$$[Pd^{II}LA]^- + e^- \rightleftharpoons [Pd^{II}LA]^{2-} \qquad (3)$$

It is implied that the ligand rather than the metal is reduced. Ligand reduction is believed to occur primarily at the azo-function. It is known that the azo-group can undergo the following two successive one-electron reductions, equation (4), in aprotic solvents.[12-17]

$$[\text{-N=N-}] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\text{-N}\overset{\cdots}{-}\text{N-}]^- \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\text{-N-N-}]^{2-} \qquad (4)$$

In bivalent alkaline-earth metal salts of sulphonated arylazo-2-naphthol [18] the redox processes (4) occur near —0.8 and —1.3 V. We have examined [19] the redox electrochemistry of groups of complexes of type [PdLD] and [PdAD] where D is a bidentate ligand such as diketonate, triazine-1-oxide, *etc.* These complexes uniformly display a *single* reversible one-electron reduction at, for [PdLD], *ca.* —0.8 V and for [PdAD], *ca.* —1.0 V. Thus L is reduced more readily than A. The two one-electron reductions in [PdLA] are therefore due to addition of one electron to the azo-group of L [couple (2)] and one electron to that of A [couple (3)]. Consideration of substituent effects strengthens this assignment. For a given L, change of substituents (*para* with respect to azo-group) in the ring A brings about increasing cathodic shift of E_{298}° of couple (3) in the order H, Me, OMe [compare (1a), (1b), and (1f)], as expected from the Hammett relation.[13] Couple (2) is also affected but the magnitude of the effect is much smaller.

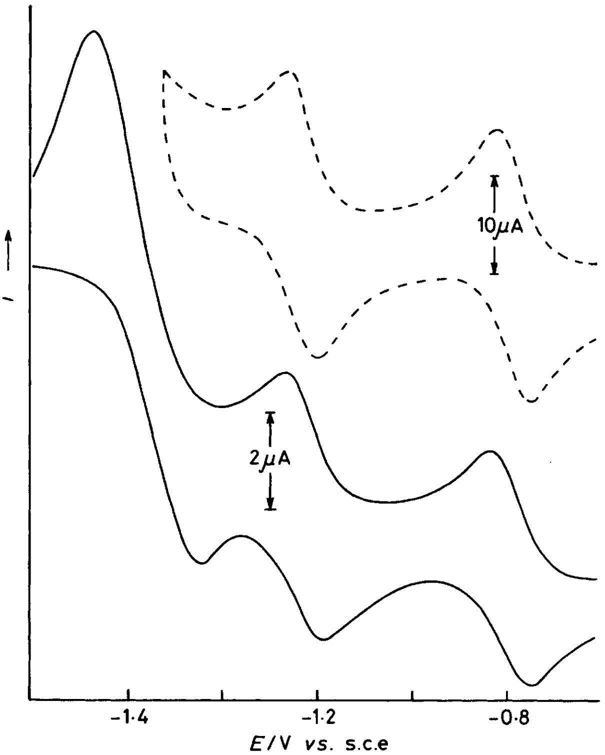


FIGURE 2 Cyclic voltammograms of [PdL^{1}A^{15}] in CH_3CN, 0.1 mol dm^{-3} in [NEt$_4$][ClO$_4$] at an h.m.d.e. (——), and at a platinum electrode (— — —); scan rate 50 mV s^{-1}, 298 K, solute concentration *ca.* 10^{-3} mol dm^{-3}

At potentials more negative of couple (3) one more electron could in principle be added to each of the two $[\text{-N}\overset{\cdots}{-}\text{N-}]^-$ groups. As shown in the next section, metal reduction intervenes before this level of reduction is achieved.

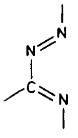
Functional groups (4a) and (4b) present in L and A respectively are formally isoelectronic with the α-di-imine function (4c). Planar complexes of d^8 metal(II) ions with (4c) display [20] successive reversible reductions of the ligand. The description of electron addition to [PdLA] along similar lines may not be appropriate since the azo-group localises the reducing equivalents.[14] The e.s.r. spectra of reduced [PdLA] species would be interesting and are under investigation.

TABLE 3

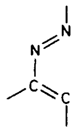
Cyclic voltammetric data * at 298 K in acetonitrile

Compound	Couple (2) $-E_{298}^{0}$ (ΔE_p)	Couple (3) $-E_{298}^{0}$ (ΔE_p)	Couple (5) $-E_{298}^{0}$ (ΔE_p)
(1a)	0.76 (65)	1.19 (71)	1.46 (162)
(1b)	0.78 (68)	1.23 (59)	1.53 (209)
(1c)	0.75 (75)	1.23 (73)	1.57 (160)
(1d)	0.82 (58)	1.29 (64)	1.58 (168)
(1e)	0.78 (78)	1.30 (70)	1.58 (110)
(1f)	0.81 (72)	1.29 (80)	1.42 (198)
(1j)	0.78 (62)	1.22 (59)	1.55 (220)
(1k)	0.76 (74)	1.23 (77)	1.53 (120)
(1l)	0.71 (63)	1.15 (64)	1.46 (113)
(1m)	0.80 (58)	1.26 (62)	1.59 (215)
(1n)	0.78 (68)	1.32 (60)	1.60 (117)
(1o)	0.78 (70)	1.20 (73)	1.47 (107)

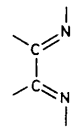
* $E_{298}^{0} = 0.5(E_{pc} + E_{pa})$; E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively; E_{298}^{0} (referenced to s.c.e.) in V and ΔE_p in mV; scan rate 50 mV s^{-1}. Solute concentration *ca.* 1 × 10^{-3} mol dm^{-3}; 0.1 mol dm^{-3} [NEt$_4$][ClO$_4$] as supporting electrolyte. E_{298}^{0} data of couples (2) and (3) are collected at a Pt electrode and couple (5) at an h.m.d.e. Couples (2) and (3) were also studied at an h.m.d.e. and the results are nearly identical to those at the Pt electrode.



(4a)



(4b)



(4c)

Metal reduction. The couple near —1.5 V has ΔE_p = 80—200 mV. The height of the cathodic peak is nearly three times those of the one-electron couples considered earlier (the current height for a two-electron process is expected to be approximately $2\sqrt{2}$ times that of an one-electron process). The anodic peak is smaller than the cathodic peak. The results suggest a two-electron quasi-reversible reduction followed by chemical reaction as in (5) and (6). In couple (5) the metal is reduced and

$$[\text{Pd}^{\text{II}}\text{LA}]^{2-} + 2e^- \rightleftharpoons [\text{Pd}^0\text{LA}]^{4-} \qquad (5)$$

$$[\text{Pd}^0\text{LA}]^{4-} \xrightarrow{k_f} \text{products} \qquad (6)$$

the lifetime of the unstable Pd^0 complex is long enough for electrochemical detection during scan reversal. Assignment to ligand reduction is excluded as follows. The addition of two electrons to the two $[\text{-N}\overset{\cdots}{-}\text{N-}]^-$ groups of [PdLA]$^{2-}$ at the same potential is unlikely. Further, the E_{pc} of couple (5) is only 300 mV more negative than that of couple (3). Finally, [PdLD]$^-$ formed by one-electron azo-reduction of [PdLD] undergoes [19] a similar two-electron $Pd^{II} \rightarrow Pd^{0}$ reduction at *ca.* −1.5 V.

The direct conversion of Pd^{II} to Pd^{0} is documented in, for example, amine and cyanide complexes in aqueous medium [21] and in phosphine complexes in aprotic solvents.[22] Evidently in these cases as well as in the complexes under study the palladium(I) intermediate is thermodynamically unstable relative to both palladium(II) and palladium(0). Generally, discrete molecular palladium(I) species are very rare [23] outside the realm of metal–metal bonded compounds.[24]

EXPERIMENTAL

Chemicals and Starting Materials.—These were procured or synthesised as before.[10] Substituted azobenzenes were prepared according to reported methods.[25] Tetraethylammonium perchlorate was obtained from tetraethylammonium bromide using a literature method.[26] Acetonitrile for electrochemical use was prepared by purifying the commercial solvent with CaH_2 treatment, followed by repeated distillation over P_4O_{10} and then over a Li_2CO_3–$KMnO_4$ mixture.

Commercially available analytical grade solvents were used for spectroscopic measurements.

Measurements.—Spectroscopic data were obtained using the following instruments: i.r. spectra, Beckman IR-20A spectrophotometer; electronic spectra, Cary 17D or Pye Unicam SP8-150 spectrophotometers; ^1H n.m.r. spectra, Varian T-60A or Varian EM-390 spectrometers. Electrochemical measurements were done using a PAR model 370-4 electrochemistry system. Cyclic voltammetry was performed using a PAR 174A polarographic analyser, 175 universal programmer, and REOO74 XY recorder. All experiments were done under a nitrogen atmosphere in a three-electrode configuration. The working electrode was either a Metrohm E 410 hanging mercury drop electrode or planar platinum of Beckman 39273 type. The results reported are uncorrected for junction potentials. Controlled-potential coulometry required the PAR 173 potentiostat, PAR 179 digital coulometer, and PAR 377A cell system taken in conjunction with a platinum-wire gauge working electrode.

Synthesis of Compounds.—Complexes $[Pd_2Cl_2A_2]$ were prepared according to the reported method.[3] [PdClAB] was generated *in situ* for ^1H n.m.r. work by mixing $[Pd_2Cl_2A_2]$ and Lewis bases (B) in 1 : 2 ratios in $CDCl_3$.[8] All complexes of type (1) were prepared by using similar methods. Specific details are given below for one representative case. In the reported [11] synthesis of $[PdL^2A^1]$, Na_2CO_3 was used as base; in the present method this has been eliminated and other changes are made resulting in much improved yield.

(α-*Phenylazoacetaldoximato*-NN)(2-*phenylazophenyl*-C^1N')-*palladium*(II), (1a).—To di-μ-chloro-bis[(2-phenylazophenyl-C^1N')palladium(II)] (258.4 mg, 0.4 mmol) in benzene (50 cm³) was added a solution of phenylazoacetaldoxime (130 mg, 0.8 mmol) in benzene (10 cm³). The resulting solution was heated to boiling (353 K) and poured into water (20 cm³). The mixture was stirred for *ca.* 30 min. The benzene layer was separated and filtered, and the violet filtrate was chromatographed on alumina using benzene as eluant. The violet fraction was evaporated to *ca.* 10 cm³ and hexane (10 cm³) was added. On scratching, crystals separated out and were collected by filtration (yield *ca.* 75%).

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