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2-(ARYLAZO)ARYL DERIVATIVES OF MERCURY, PALLADIUM, PLATINUM, NICKEL AND MANGANESE

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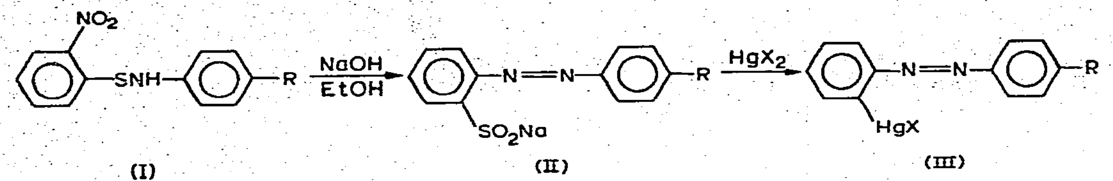
Summary

Several new [2-(arylazo)aryl] mercury derivatives have been isolated from the reactions of the corresponding azobenzene-2-sulphinates (which are easily prepared) and mercuric chloride. The mercurials can have a variety of ring substituents, which increase their value as arylating agents. Thus, the action of these compounds on $PdCl_2$ leads to the expected chelating C^2, N'-bonded azobenzene—palladium derivatives in high yield. Bis[2-(phenylazo)phenyl] mercury reacts with the phosphine complexes $(R_3P)_2MCl_2$ (M = Pd or Pt) to produce *trans*-$(R_3P)_2MCl(C_6H_4N_2Ph)$, and with nickelocene to produce (h^5-cyclopentadienyl) (phenylazophenyl-C^2, N')nickel(II). [2-(phenylazo)phenyl] mercuric halides react with $Mn(CO)_5Cl$ to form tetracarbonyl(phenylazophenyl-C^2, N')-manganese(I) in good yields.

The NMR spectra of the above compounds are interpreted for the various substitution patterns of the two phenyl rings and, along with their IR spectra, can be used for identification purposes. The methyl group chemical shifts of *ortho*-methyl substituted derivatives are dependent on the bonding mode, and can be used to determine whether the azobenzene group is monodentate or C^2, N')-bidentate.

Introduction

In a recent paper we described the facile preparation of a number of [2-(arylazo)phenyl] mercury compounds [1]. The route, which produces high yields from readily available material, involves the base-promoted rearrangement of 2-nitrobenzenesulphenanilide derivatives (I) to the corresponding azobenzene-2-sulphinates (II). Subsequent treatment of (II) by mercuric halide produces the 2-(halomercuri)azobenzene derivatives, (III).



(R = H, Me, OMe or Cl)

Facile and specific cleavage of the mercury—carbon bonds of (III) by halogens or nitrosyl chloride demonstrated the value of these compounds as synthetic reagents.

Whilst many azobenzene derivatives of transition metals are known, none appears to seriously rival the potential of the mercury compounds, (III), in such synthetic processes. This is mainly because both their preparations and reactions can be difficult and unpredictable, and lack specificity [1, 2].

We report here the isolation of several new [2-(arylazo)aryl] mercury compounds with a variety of substituents on both aromatic rings, thus greatly extending the known range of compounds of type (III). Moreover, these reagents have been used to prepare 2-(arylazo)aryl derivatives of various transition metals, and in many cases make the best route to these compounds.

Characteristic features of the IR and NMR spectra of all the derivatives can be assigned and interpreted for the various aryl substitution patterns. This has analytical value when the stereochemistry of the compounds is in doubt, as is frequently the case when less specific routes are employed.

Results and discussion

The most critical step in the formation of the [2-(arylazo)aryl] mercury compounds is the rearrangement of (I) to (II). From a study of the rearrangement mechanism of *para*-substituted sulphenanilides [(I) R = H or OMe] [3] and our previoius work [1], we were able to suggest that this step should proceed for many other substituent groups provided their Hammett σ-constants [4] were not too high. We have now extended this reaction to examples with methyl- or bromo-substituents on the *ortho*- or *meta*-positions of ring 2* and also with an additional chloro-substituent on ring 1, demonstrating the versatility of this step. The base-promoted rearrangement of some *o*- and *m*-substituted sulphenanilides has been noted previously [5], but the wrong products deduced. The sulphinates produced in the above rearrangement reacted smoothly with mercuric chloride to produce the 2-(chloromercuri)azobenzene derivatives. The new compounds are listed in Table 1. Although this reaction proceeds in high yield, the formation of the orange or red crystalline products was accompanied by production of some mercury(I) chloride. This has been noted before for the Peter's reaction [6], and taken to imply reduction of $HgCl_2$ by sulphurous acid formed during the SO_2 elimination process. We observed very little reduction, however, on passing SO_2 through a refluxing ethanol solution of mercury(II) chloride.

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*We refer to the aryl group which is at some stage bonded to the metal atoms in our reaction sequences as *ring one*, and the other, non-coordinated ring as *ring two* throughout.

TABLE 1

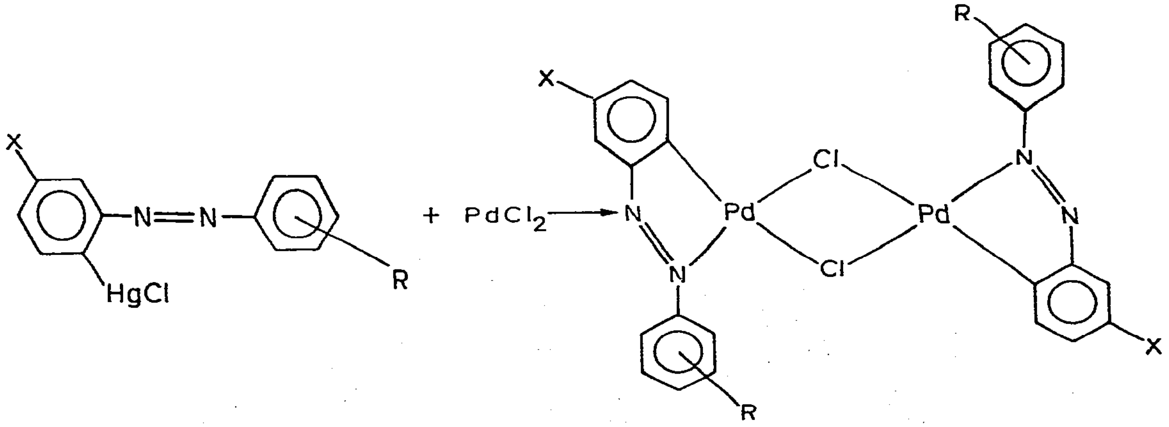
ANALYTICAL AND PHYSICAL DATA FOR THE NEW [2-(ARYLAZO)ARYL] MERCURY COMPOUNDS

Compound	M.p. (°C)	Yield[a] (%)	Analysis found (calcd.) (%)			ν(Hg—Cl)[b] (cm^{-1})
			C	H	N	
$(2'\text{-}MeC_6H_4N_2C_6H_4)HgCl$	189-191	50	36.45 (36.21)	2.64 (2.57)	6.41 (6.50)	326
$(3'\text{-}MeC_6H_4N_2C_6H_4)HgCl$	188-190	57	36.22 (36.21)	2.66 (2.57)	6.31 (6.50)	328
$(2'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)HgCl$	209-214[c]	51	33.44 (33.53)	2.26 (2.16)	5.97 (6.01)	329 (325sh, 320sh)
$(3'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)HgCl$	224-228[c]	66	33.54 (33.53)	2.28 (2.16)	6.03 (6.01)	326 (328sh, 316sh)
$(4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)HgCl$	215-217	67	33.44 (33.53)	2.13 (2.16)	6.03 (6.01)	326 (323sh)
$(3',5'\text{-}Br_2C_6H_3N_2C_6H_4)HgCl$	252-257[c]	37	25.21 (25.06)	1.33 (1.23)	5.14 (4.87)	326 (321sh, 314sh)
$(3',5'\text{-}Br_2C_6H_3N_2C_6H_3\text{-}4\text{-}Cl)HgCl$	273-280[c]	42	23.59 (23.65)	1.05 (0.99)	4.39 (4.59)	334 (330sh, 325sh)

[a] Overall yield for the reaction sequence 2-nitroarenesulphenyl chloride to [2-(arylazo)aryl] mercuric chloride. [b] KBr disc. [c] Melting points were not sharp: see text.

The melting points of some of the mercurials in Table 1 were not sharp. A possible explanation of this might be the formation of liquid crystals [7], as some related azobenzene derivatives have been observed to display this phenomenon. We cannot, however, rule out the possibility that spontaneous symmetrisation caused the broad melting range observed.

[2-(Arylazo)aryl] mercuric chlorides react with $PdCl_2$ in methanol to give quantitative yields of the chloro-bridged azobenzene palladium derivatives (IV) (see Table 2). The reactions between azobenzene and $PdCl_2$ [8] or Na_2PdCl_4 [9]



(IV)

($X = H$; $R = H$ and $X = Cl$; $R =$ 2-Me, 3-Me, 4-Me, or 3,5-Br_2)

are known to produce (IV) ($X = R = H$). We have repeated these reactions and from the $PdCl_2$ route we also isolated small quantities of dichlorobis(azobenzene)palladium(II). This compound has been previously isolated from the reac-

TABLE 2

GENERAL PHYSICAL DATA, AND ANALYSES OF 2-(ARYLAZO)ARYL COMPLEXES OF PALLADIUM AND PLATINUM

Compound	Colour	M.p. ($^\circ$C)	Analysis found (calcd.) (%) C	H	N	ν(M—Cl)[a] (cm^{-1})
$(C_6H_5N_2C_6H_5)_2PdCl_2$	Orange	195-204(dec)	53.12	3.78	10.29	337
			(53.21)	(3.72)	(10.34)	
$[(C_6H_5N_2C_6H_4)PdCl]_2$	Maroon	272-275(dec)	44.97	2.91	8.42	
			(44.61)	(2.81)	(8.67)	
$[(2'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)PdCl]_2$	Orange	262-267(dec)	42.03	2.80	7.29	
			(42.03)	(2.71)	(7.54)	
$[(3'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)PdCl]_2$	Maroon	285-300(dec)	41.93	2.79	7.63	
			(42.03)	(2.71)	(7.54)	
$[(4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)PdCl]_2$	Maroon	285-295(dec)	42.01	2.99	7.77	
			(42.03)	(2.71)	(7.54)	
$[(3',5'\text{-}Br_2C_6H_3N_2C_6H_3\text{-}4\text{-}Cl)PdCl]_2$	Maroon	310-320(dec)	27.86	1.34	5.10	
			(27.97)	(1.17)	(5.44)	
$(C_6H_5N_2C_6H_4)Pd(PEt_3)_2Cl$[b]	Orange	116-118	52.07	6.92	5.44	298
			(51.54)	(7.03)	(5.01)	
$(2'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)Pd(PEt_3)_2Cl$	Orange-red	130-132	49.49	6.87	4.53	299 (294sh)
			(49.40)	(6.63)	(4.61)	
$(3'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)Pd(PEt_3)_2Cl$	Orange-red	165-167	49.30	6.76	4.49	298 (292sh)
			(49.40)	(6.63)	(4.61)	
$(4'\text{-}MeC_6H_4N_2C_6H_3\text{-}4\text{-}Cl)Pd(PEt_3)_2Cl$	Orange-red	154-156	49.53	6.90	4.89	295 (285sh)
			(49.40)	(6.63)	(4.61)	
$[(C_6H_5N_2C_6H_4)PtCl]_2$	Purple	258-265(dec)	35.62	2.33	7.10	
			(35.00)	(2.20)	(6.80)	
$(C_6H_5N_2C_6H_4)_2Pt(PEt_3)_2Cl$	Orange	129-131	44.71	5.88	4.70	265 (276sh)
			(44.48)	(6.07)	(4.32)	
$(C_6H_5N_2C_6H_4)Pt(PPh_2Me)Cl$	Maroon	196-198	49.14	3.77	4.55	286
			(49.06)	(3.62)	(4.57)	
$(C_6H_5N_2C_6H_4)Pt(PPh_2Me)_2Cl$	Maroon	154-156	56.45	4.53	3.27	299br
			(56.20)	(4.34)	(3.45)	

[a] KBr disc. [b] Found: Cl, 5.79. Calcd.: Cl, 5.92%.

tion of $(PhCN)_2PdCl_2$ with azobenzene [10], and is a suggested precursor of (IV) in the azobenzene/$PdCl_2$ reaction. Substituted azobenzenes and K_2PdCl_4 react to yield a mixture of isomers of the C^2, N'-bonded azobenzene palladium dimer [2, 11], whereas the mercurial route reported here appears to be quite specific and is the preferred route to (IV).

The transfer of aryl groups from mercury to palladium(II) is a key step in the $PdCl_2$ catalysed arylation of olefins by arylmercuric halides. These reactions have been studied in depth by Heck [12], who reported that if the aryl group contains a strong donor-atom as substituent, then the catalytic addition fails and an isolable organopalladium compound is the end-product. In keeping with this, we failed to arylate styrene using [2-(phenylazo)phenyl] mercuric chloride and $PdCl_2$ in methanol, but isolated (IV) ($R = X = H$) instead. (It should be noted, however, that the transfer of *ortho*-$C_6H_4CH_2NMe_2$ from Pd to styrene in acetic acid solution has recently been found [13]).

The platinum analogue of (IV) ($R = X = H$) has been isolated from the reaction between azobenzene and K_2PtCl_4 [8], though we have found this process to be slow and to give poor yields. The reaction between azobenzene and $PtCl_2$ is even slower, though the formation after about six weeks of some di-μ-chloro-bis(phenylazophenyl-C^2, N')diplatinum and the detection of HCl indicated that the reaction was proceeding. We expected the transfer of 2-(phenylazo)phenyl groups from mercury to platinum(II) chloride to provide a superior route to platinum analogues of (IV), but at room temperature no reaction was observed after 24 h. Refluxing the methanol solution led only to decomposition to platinum metal. Finely divided platinum metals have been reported to decompose diarylmercurials [14], so the decomposition may be auto-catalytic.

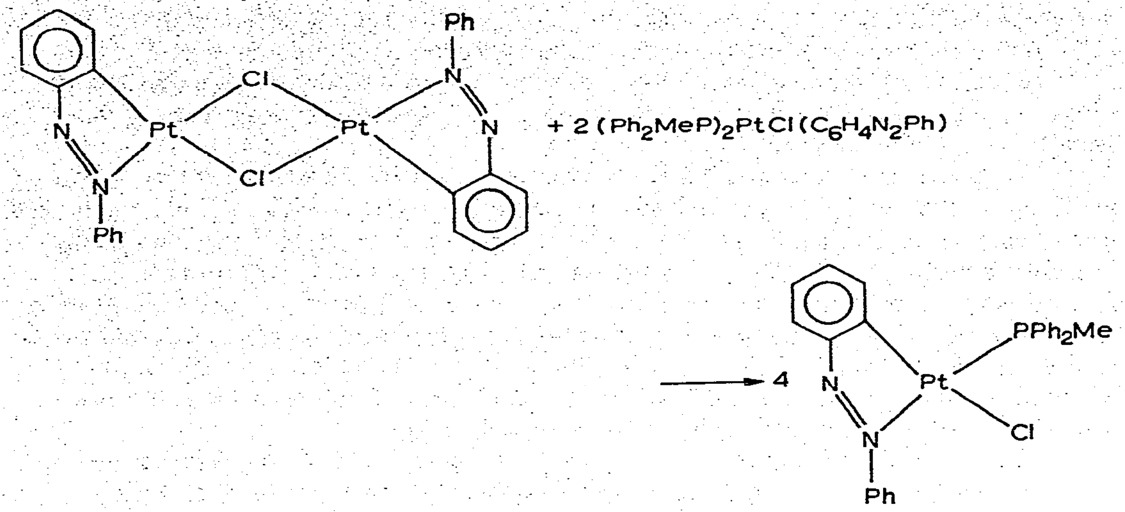
This behaviour difference between platinum and palladium derivatives is further emphasised in the preparation of the triethylphosphine complexes V by the reaction sequence below. The yield of V ($M = Pd$) was much greater

$$(PhN_2C_6H_4)_2Hg + (Et_3P)_2MCl_2 \rightarrow (PhN_2C_6H_4)M(PEt_3)_2Cl + (PhN_2C_6H_4)HgCl$$

$$(M = Pd \text{ or } Pt) \qquad\qquad (V)$$

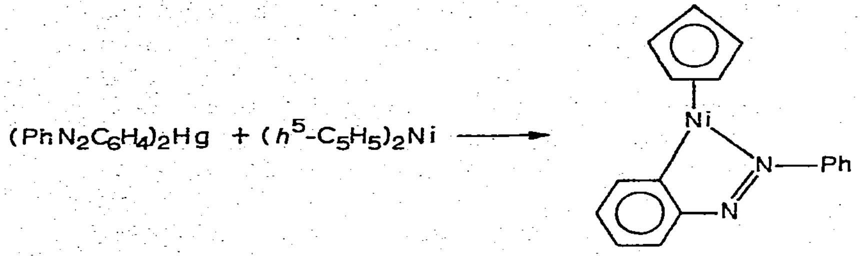
than V ($M = Pt$), and the formation of some metallic mercury and azobenzene was observed in the latter case. The transfer of aryl groups from mercury to platinum—, palladium— or nickel—phosphine complexes of this type is well known [15], but the poorer yield of the platinum derivatives in the present example was unexpected. The observation of "virtual coupling" in the ^1H NMR spectra [16] of complexes V, and the values of $\nu(M-Cl)$ from their IR spectra (see Table 2), established their structure as *trans*. Complex V ($M = Pd$) has been previously prepared from the action of triethylphosphine on (IV) ($X = R = H$), and its crystal structure determined [17].

The addition of one equivalent of tertiary phosphine to platinum or palladium complexes of type (IV) is known to cleave the bridge and produce monomers of type (VI) [2]. We observe that (VI) is rapidly formed simply on mixing the correct analogues of (IV) and (V).



(VI)

The reactions between bis[2-(phenylazo)phenyl] mercury and nickelocene in refluxing benzene produces high yields of (phenylazophenyl-C^2, N')(h^5-cyclopentadienyl)nickel (VII). The expected by-product, [2-(phenylazo)phenyl] (h^1-cyclopentadienyl)mercury was not isolated, but cyclopentadienyls of mercury

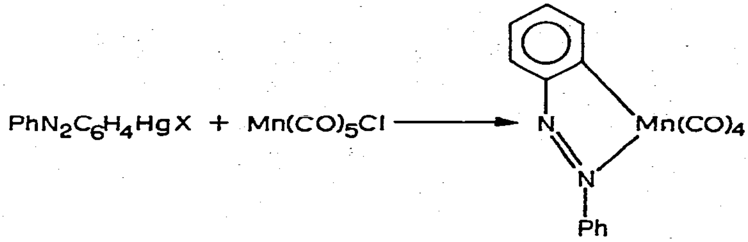


(VII)

are known to be unstable [18], and unsymmetrical diorganomercurials slowly symmetrise [19]. Some bis[2-(phenylazo)phenyl] mercury was in fact isolated from the reaction mixture. Complex (VII) has been prepared from the action of azobenzene or 2-haloazobenzene on nickelocene, but in inferior yield [20].

Both the above routes to (VII) probably proceed via a mechanism involving coordination of nitrogen to nickel and $\pi \rightarrow \sigma$ conversion of a cyclopentadienyl ligand. The next steps will differ, and involve cleavage of the Ni—(h^1-C_5H_5) bond by either mercurial or halide. There are precedents for both using triphenylphosphine as nucleophile. Organic halides lead to (h^5-C_5H_5)(Ph_3P)NiX [21], whereas dimethylmercury produces (h^5-C_5H_5)(Ph_3P)NiMe [22].

The formation of organomanganese carbonyl compounds from pentacarbonylmanganese halides and other organometallic reagents has received little attention, though transfer of an organic group to manganese from, for example, C_6F_5MgBr [23] or allyltrimethyltin [24] is documented. We find that [2-(phenylazo)phenyl] mercuric halide and $(CO)_5MnCl$ produce good yields of tetracarbonyl-(phenylazophenyl-C^2, N')-manganese, (VIII). Complex (VIII) has been prepared previously using azobenzene itself [11, 25], though yields are actually lower than by our method. There is evidence that the reaction between azobenzene and methylmanganese pentacarbonyl, which gives high yields of (VIII), proceeds via initial nucleophilic attack at the *ortho* position of the aromatic ring [11]. This mechanism could operate in our case, but the possibility of CO displacement by a nitrogen donor atom followed by mercuric halide elimination cannot be discounted.



(VIII)

NMR spectra

Complete or partial analyses of the ${}^1H$ NMR spectra of a few azobenzene—transition-metal complexes have been reported [25, 26]. The spectra obtained from our mercury derivatives are more difficult to analyse, as the chemical shifts of the aromatic protons span a smaller range. Low solubility of some derivatives further complicates the issue.

Nevertheless, complete analyses are possible for some of the more highly substituted derivatives. Line diagrams of examples are shown in Fig. 1. Comparison with these spectra, and also with the better-resolved spectra of palladium

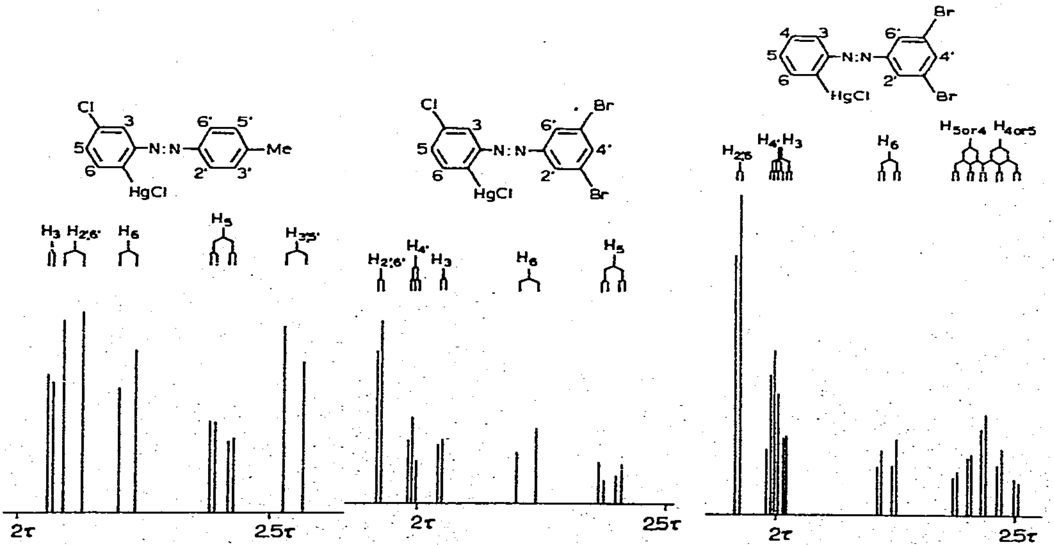
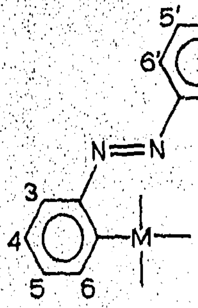


Fig. 1. Line diagrams of the aromatic regions of the ${}^1H$ NMR spectra of some 2-(arylazo)aryl derivatives (220 MHz).

TABLE 3

PROTON NMR SPECTRA

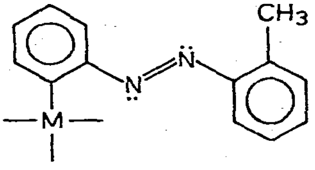


Compound	Chemical Shifts (τ)										$^3J(^1H-^{199}Hg)$ (Hz)	Solvent	Temp. (°C)
	H_3	H_4	H_5	H_6	$H_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$	Me			
$(4'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})HgCl$[a]	2.06d		2.41dd	2.21d	2.10d	2.55d		2.55d	2.10d	7.58s[c]	203	$(CD_3)_2SO$	+61
$(3'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})HgCl$[a]	2.04d		2.40dd	2.19d	2.18[f]		2.55dt	2.48t	2.19[f]	7.57s[c]	201	$(CD_3)_2SO$	+61
$(2'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})HgCl$[a]	2.14d		2.42dd	2.18d		*e*	*e*	*e*	*e*	7.29s[c]	199	$(CD_3)_2SO$	+61
$(3',5'\text{-Br}_2C_6H_3N{=}NC_6H_3\text{-4-Cl})HgCl$[a]	2.07d		2.37dd	2.17d	1.87d		1.97t		1.87d			$(CD_3)_2SO$	+61
$(3',5'\text{-Br}_2C_6H_3N{=}NC_6H_4)HgCl$[a]	1.99dd	2.38td	2.42td	2.20dd	1.88d		1.97t		1.88d			$(CD_3)_2SO$	+61
$(4'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})_2Pd_2Cl_2$[b]	1.97d		2.69dd	2.22d	2.23d	2.62d		2.62d	2.23d	7.58s		$(CD_3)_2SO$	+70
$(3'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})_2Pd_2Cl_2$[b]	1.97d		2.70dd	2.24d	*e*		*e*	*e*	*e*	7.58s		$(CD_3)_2SO$	+70
$(2'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})_2Pd_2Cl_2$[b]	1.87d		2.58dd	2.21d		*e*	*e*	*e*	*e*	7.62s		$(CD_3)_2SO$	+70
$(4'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})Pd(PEt_3)_2Cl$[b]	2.46d		3.02dd	2.51d	2.07d	2.72		2.72d	2.07d	7.58s		CCl_4	+35
$(3'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})Pd(PEt_3)_2Cl$[b]	2.52d		3.06dd	2.55d	2.73d		2.85d(br)	*e*	*e*	7.56s		CCl_4	+35
$(2'\text{-MeC}_6H_4N{=}NC_6H_3\text{-4-Cl})Pd(PEt_3)_2Cl$[b]	2.65d		3.04dd	2.55d		*e*	*e*	*e*	*e*	7.23s		CCl_4	+35

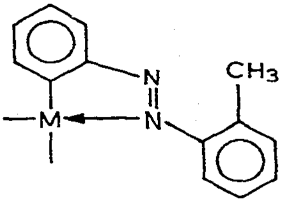
[a] Recorded at 220 MHz. [b] Recorded at 100 MHz. [c] Values for the analogous complexes[b] with H in position 4: 4'-Me, 7.64s; 3'-Me, 7.57s; 2'-Me, 6.19s. [f] Partially obscured by H_6. [e] Overlap of signals prevents assignment.

and iodine [1] derivatives, has allowed at least a partial interpretation of the more difficult spectra. Data is tabulated in Table 3. The coupling constants between *ortho* protons (ca. 8 Hz) and *meta* protons (ca. 2·5 Hz) are quite normal [27], as are the values of $^{3}J(^{1}\mathrm{H}-^{199}\mathrm{Hg})$ (ca. 200 Hz) [28]. In the chloro-substituted compounds the proton between Cl and the nitrogen is shifted well to low field compared to the other aromatic protons.

In comparing the spectra of *o*-, *m*- or *p*-methyl substituents on ring 2, we note a significant downfield shift of the methyl resonance of the *ortho*-derivatives when the ligand is monodentate and carbon-bonded only. This shift is not found in the bidentate (C^2, N'-bonded) complexes. With a *trans*-planar structure for the azobenzene moiety, the configuration of the monodentate derivatives will be that depicted in (IX). The magnetic anisotropic effect of the lone pair on nitrogen will cause the downfield shift. In the bidentate derivatives (X), this lone pair is not available.



(IX)



(X)

IR spectra

Carbon—hydrogen out of plane deformation modes can be observed for most of the derivatives near 750 cm^{-1}. These absorptions are characteristic for the substitution patterns involved [29], though we find an extra absorption band near 710 cm^{-1} from the 1,2-disubstituted aromatics. Masking of some of these absorptions occurs in the spectra of phosphine derivatives, but in general the recognition of the substitution patterns from this IR region is a simple process. Table 4 lists the relevant bands for our complexes.

Experimental

IR spectra (4000—200 cm^{-1}) were recorded on a Perkin—Elmer 225 spectrometer. NMR spectra were recorded on Varian HA 220 (220 MHz.), Varian HA 100 (100 MHz), and Jeol C-60HL (60 MHz) spectrometers. M.p.'s (corrected) were measured on a Reichert—Kofler hot-stage apparatus. Reactions were carried out under a nitrogen atmosphere where stated and no special precautions were taken during the work up of the products, all of which are air stable.

Preparation of [2-(arylazo)aryl] mercurials

These derivatives were prepared by the synthetic route previously described [1] and a typical example is given below. M.p. and analytical data are contained in Table 1.

2-(4'-Methylphenylazo)-4-chlorophenylmercuric chloride. To a cool stirred solution of 2,4-nitrochlorobenzene sulphenyl chloride (3.2930 g, 14·7

TABLE 4

C—H OUT-OF-PLANE DEFORMATION MODES FOR [2-(ARYLAZO)ARYL] METAL COMPLEXES

Compound	Ring Substitution pattern					
	1	1,2	1,3	1,4	1,3,5	1,2,4
$(C_6H_5N{=}NC_6H_4)HgCl$	774vs(br) 684s	765(sh)				
$(C_6H_5N{=}NC_6H_4)HgBr$	771s 682s	765(sh)				
$(C_6H_5N{=}NC_6H_4)HgCl$	777s 678s	761s				
$(2'\text{-}MeC_6H_4N{=}NC_6H_4)HgCl$		761s				
$(3'\text{-}MeC_6H_4N{=}NC_6H_4)HgCl$		762s	785s 683s			
$(4'\text{-}MeC_6H_4N{=}NC_6H_4)HgCl$		761s		822vs		
$(4'\text{-}MeOC_6H_4N{=}NC_6H_4)HgCl$		763s(769sh)		830vs		
$(4'\text{-}ClC_6H_4N{=}NC_6H_4)HgCl$		763s(br)		834vs		
$(3',5'\text{-}Br_2C_6H_3N{=}NC_6H_4)HgCl$		760s(769sh)			857s 746s	
$(2'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)HgCl$		760s				885m or 869m 822s
$(3'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)HgCl$			782s 680s			880s 815s
$(4'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)HgCl$				821vs(br)		880s or 869m 815(sh)
$(2'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)_2Pd_2Cl_2$		770s				882m or 865m 815s
$(3'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)_2Pd_2Cl_2$			776s 685s			880(sh) or 869m 804s
$(4'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)_2Pd_2Cl_2$				811s		879m or 869m 811s
$(2'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)Pd(PEt_3)_2Cl$		775s				888m 821s
$(3'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)Pd(PEt_3)_2Cl$			799s 694s			884m 815s
$(4'\text{-}MeC_6H_4N{=}NC_6H_3\text{-}4\text{-}Cl)Pd(PEt_3)_2Cl$				830vs(br)		881m or 861m Obscured

mmoles) in dry ether (100 ml) was added a solution of *p*-toluidine (2·7328 g, 29·6 mmoles) in ether (50 ml). The dense white preicpitate of *p*-toluidine hydrochloride was removed by filtration. Evaporation of the filtrate and recrystallisation from ethanol gave maroon needles of 2,4-nitrochlorobenzenesulphen-*p*-toluidine (4·0063 g, 90%; m.p. 140-142°, lit. [30] 137°).

This material (2.3928 g, 9.6 mmoles) dissolved in ethanol (25 ml) was added to a solution of sodium hydroxide (1.0687 g, 26.7 mmoles) in water (7.5 ml). The mixture was refluxed for 6 h. Initially the colour of the solution changed to violet, but, after a few minutes reflux, developed a dark orange colour and produced the 2-sulphinate derivative of 4-chloro-4′-methylazobenzene (96% conversion). This material (2.4353 g, 7.8 mmoles) was refluxed with mercuric chloride (2.1830 g, 8.1 mmoles) in ethanol (100 ml) for 1.5 h. Concentration and filtration of the solution followed by extraction of the residue with THF and filtration removed Hg_2Cl_2 (0.2730 g, 1.0 mmoles, characterised by spot tests). Crystallisation of the THF solution yielded deep orange needles of the product (2.8092 g, 77%; m.p. 215-217°. ex carbon tetrachloride).

Di-μ-chloro-di-(phenylazophenyl-C^2, N')dipalladium.

(a). From azobenzene [8]. A suspension of palladium chloride (1.6374 g, 9.3 mmoles) in a methanol solution (75 ml) of azobenzene (2.6085 g, 14.4 mmoles) was stirred for 48 h. The orange precipitate produced was filtered and washed with C_6H_6. Recrystallisation from hot benzene produced, on concentration, bright yellow crystals of *trans*-dichlorobis(azobenzene)palladium(II) (0.0721 g, 0.1 mmoles, 1%; m.p. 195-204°, lit. [10a] 217-218°; IR spectrum identical to an authentic sample [10]). On standing, maroon crystals of di-μ-chlorodi(phenylazophenyl-C_2, N')dipalladium [2.5162 g, 85%; m.p. 272-275° (dec.) lit. [8] 279-281° (dec.)] were subsequently deposited.

(b). From [2-(phenylazo)phenyl] mercuric chloride. A suspension of palladium chloride (0.1868 g, 1.1 mmoles) and [2-(phenylazo)phenyl] mercuric chloride [1] (0.5093 g, 1.2 mmoles) in methanol (100 ml) was stirred at room temperature for 14 h. The resultant orange precipitate was removed by filtration and washed with methanol. Evaporation of the methanol filtrate and extraction with water gave $HgCl_2$ (0.0402 g, 0.2 mmoles). Recrystallisation of the orange residue from benzene gave maroon crystals of di-μ-chloro-di(phenylazophenyl-C^2, N')-dipalladium (0.2821 g, 83%; m.p. and IR spectrum identical with an authentic sample).

Physical and analytical data for compounds similarly prepared are given in Table 2.

Di-μ-chloro-di(phenylazophenyl-C^2,N')diplatinum

A suspension of platinum dichloride (0.8075 g, 3.0 mmoles) in a methanol solution (100 ml) of azobenzene (0.8879 g, 4.9 mmoles) was stirred for 6 weeks. The colour gradually darkened to maroon, and filtration removed unreacted $PtCl_2$ (0.7063 g, 2.6 mmoles). The solvent was removed from the filtrate leaving a viscous black liquid. (The presence of hydrogen chloride was noticed). Extraction of the viscous liquid with hot benzene (75 ml) gave a solution which yielded glistening purple crystals of di-μ-chloro-di(phenylazophenyl-C^2, N')-diplatinum (0.0372 g, 3%; m.p. and IR spectrum identical with an authentic sample [8]).

trans-Chloro[2-(phenylazo)phenyl] bis(triethylphosphine)platinum(II)

Method(a). To a suspension of di-μ-chloro-di(phenylazophenyl-C^2, N')-diplatinum (0.2208 g, 0.2 mmoles) in benzene (40 ml), under nitrogen, was added triethylphosphine (0.12 g, 0.4 mmoles) by syringe. The solution was stirred for 10 min at 60°. Removal of solvent and recrystallisation from hexane produced orange plates of *trans*-chloro[2-(phenylazo)phenyl] bis(triethylphosphine)-platinum(II) (0.2771 g, 86%; m.p. 129-131°).

Method (b). Bis[2-(phenylazo)phenyl] mercury [1] (0.2962 g, 0.53 mmoles) was added to a solution of *cis*-dichlorobis(triethylphosphine)platinum(II) in ethanol (35 ml). Refluxing for 19 h produced a small amount of metallic mercury (0.0018 g, 0.009 mmoles). Concentration and cooling of the solution produced feathery orange crystals of [2-(phenylazo)phenyl] mercuric chloride (0.1628 g, 0.39 mmoles) and colourless crystals identified, by m.p. and IR, as *cis*-dichlorobis-(triethylphosphine)platinum(II) (0.0260 g, 0.05 mmoles) both of which were removed by filtration.

The ethanol was removed from the filtrate producing a brown oil. Addition of hot petroleum ether (b.p. 40-60°) followed by filtration, produced more *cis*-dichlorobis(triethylphosphine)platinum(II) and a filtrate which, on removal of solvent and subsequent sublimation, produced azobenzene (0.0015 g, 0.0085 mmoles). The residue from the sublimation was dissolved in hexane and yielded orange plates of *trans*-chloro[2-(phenylazophenyl] bis(triethylphosphine)platinum(II) (0.0972 g, 29%; m.p. and IR identical with those above).

trans-Chloro[2-(phenylazo)phenyl] bis(triethylphosphine) palladium(II)

Bis[2-(phenylazo)phenyl] mercury (0.1160 g, 0.27 mmoles) was added to a solution of dichlorobis(triethylphosphine)palladium(II) in ethanol (30 ml). The solution was refluxed for 24 h. Concentration, cooling and filtration of the solution produced [2-(phenylazo)phenyl] mercuric chloride (0.0710 g, 0.17 mmoles), identified by comparison of m.p. and IR with an authentic sample.

Removal of the ethanol from the filtrate and recrystallisation from hexane gave orange plates of *trans*-chloro[2-(phenylazo)phenyl] bis(triethylphosphine)-palladium(II) (0.1287 g, 85%; m.p. 116-118°, IR identical with that of an authentic sample).

(h^5-cyclopentadienyl)(phenylazophenyl-C^2, N')-nickel(II)

To a solution of freshly sublimed nickelocene (0.1412 g, 0.7 mmoles) in benzene (50 ml) was added bis[2-(phenylazo)phenyl] mercury (0.3898 g, 0.7 mmoles). The solution was refluxed under nitrogen for 18 h by which time the colour was deep blue. Chromatography of this solution on neutral Alumina eluting with benzene/hexane mixture (1/1) produced first bis[2-(phenylazo)-phenyl] mercury (0.0188 g, 0.02 mmoles) followed by a blue band which on recrystallisation from petroleum ether (b.p. 40-60°) gave deep blue crystals of h^5-cyclopentadienyl(phenylazophenyl-C^2, N')nickel (0.2006 g, 91%; mol. wt. found (mass spectrometric, ^{58}Ni) 304, mol. wt. calcd., 304; m.p. 118-120° and NMR spectrum identical to the reported values).

Tetracarbonyl(phenylazophenyl-C^2, N')-manganese(I)

A solution of manganese pentacarbonyl chloride [31] (0.0550 g, 0.24

mmoles) and [2-(phenylazo)phenyl]mercuric iodide [1] (0.1249 g, 0.24 mmoles) in benzene (50 ml) was refluxed under nitrogen for 20 h. Removal of solvent, extraction with petroleum ether (B.p. 40-60°) and sublimation of this extract (40°/0.1 mm) produced maroon crystals of tetracarbonyl(phenylazophenyl-C^2, N')-manganese (0.0598 g, 70%; mol. wt. found (mass spectrometric) 348, mol. wt. calcd., 348; IR and NMR spectra identical to those previously reported [25]).

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