Cyclometallation Reactions. Part 17.[1] Comparative Studies of the Manganation and Palladation of Some Substituted Azobenzenes

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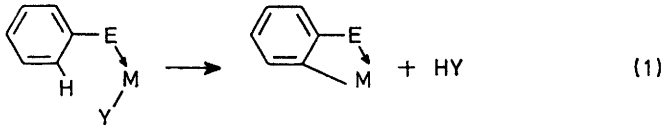
Comparative studies of the manganation {with $[MnMe(CO)_5]$} and palladation (with $PdCl_2$) of several substituted azobenzenes have demonstrated that these complexes behave as nucleophilic and electrophilic reagents, respectively. Assignment of the isomeric structures of the products is facilitated by ^{19}F n.m.r. spectroscopy using fluoroazobenzenes. Metallation of the 2- and 4-substituted azobenzenes $XC_6H_4N{:}NPh$ may give products in which the azobenzene has been metallated either in the Ph ring [isomer (a)] or in the substituted ring [isomer (b)]; 3-substituted azobenzenes may give complexes in which the Ph ring has been metallated [isomer (a)], or isomers in which metallation occurs at either of the carbons *ortho* to the azo-function in the substituted ring [isomers (b) or (c)]. Using $XC_6H_4N{:}NC_6F_5$ the C_6F_5 group is not metallated, and the only complexes formed have structures corresponding to isomer (b) (with 2- or 4-substituted compounds), or to isomers (b) and (c) (in the 3-substituted series). Electron-withdrawing substituents activate the aromatic ring to attack by $[MnMe(CO)_5]$, while electron-donating substituents activate the ring towards electrophilic attack by $PdCl_2$.

An important reaction in the chemistry of ligands containing aromatic groups bonded to donor atoms is the cyclometallation (or *ortho*-metallation) reaction,[2] in which aryl carbon–metal σ bonds are formed *via* displacement of an *ortho*-hydrogen by a metal atom [equation (1)]. The complexes so formed may be stable, or may



(1)

act as intermediates in catalytic reactions leading to products resulting from the activation of the *ortho*-C–H bond by the metal. Reactions involving azobenzene were some of the first reported, have been the most extensively studied, and have been the subject of several reviews.[3–5]

Metallation of azobenzene has been achieved using appropriate complexes of nearly all the transition elements, and a brief study of the efficiency of various leaving groups from manganese has recently been reported.[6] In the palladation reaction, it has been generally assumed that substitution occurs by electrophilic attack on the aromatic ring by the metal complex, somewhat akin to the well known mercuration of aromatic compounds.[7] Indeed, direct mercuration of azobenzene has recently been achieved by two groups of workers,[8,9] and the preparation of other complexes containing metallated azobenzenes using this reagent is facilitated.[10] Apart from the formal resemblance of palladium(II) chloride to mercury(II) chloride (or acetate) in this reaction, evidence for the process being electrophilic in character comes from the results of metallation of asymmetrically substituted azobenzenes, such as 4-dimethylaminoazobenzene, in which the substituted (or electron-rich) ring is preferentially palladated.[7]

Although this is a reasonable interpretation of the limited number of reactions of this type that have been reported, it seems unlikely that a low-valent transition-metal complex, such as $[MnMe(CO)_5]$, would behave as an electrophile. Indeed, metallation reactions involving phosphorus-donor ligands have been described as nucleophilic attacks on the aryl group.[11] To resolve this point, we have investigated the behaviour of variously substituted azobenzenes in reactions with $[MnMe(CO)_5]$ and with $PdCl_2$, which may be regarded as having respectively 'nucleophilic' and 'electrophilic' character, and which afford manganated and palladated complexes. We have also used azobenzenes which are substituted in the 3 positions, *i.e.* either *ortho* or *para* to the expected site of metallation, rather than the 4-substituted derivatives used in previous investigations. In this way we hoped to relate more directly any electronic effects of the substituent on the reaction. At the same time, we have also studied the effect of blocking completely one ring towards substitution by introducing the C_6F_5 group on one side of the azo-linkage. Although we have previously reported the formation of metallated derivatives by fluorine-abstraction reactions,[12] none of these products was isolated during the present work. Some parts of this study have been communicated previously.[13]

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[1] Part 16, M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J.C.S. Dalton*, 1976, 81.
[2] M. I. Bruce, *Angew. Chem.*, 1977, **89**, 75; *Angew. Chem. Internat. Edn.*, 1977, **16**, 73.
[3] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.
[4] A. J. Carty, *Organometallic Chem. Rev.*, 1972, **A7**, 191 (see particularly pp. 225—243).
[5] M. I. Bruce and B. L. Goodall in 'The Chemistry of Hydrazo, Azo and Azoxy Groups,' ed. S. Patai, Wiley, New York, 1975, vol. 1, pp. 259—311.
[6] R. L. Bennett, M. I. Bruce, and F. G. A. Stone, *J. Organometallic Chem.*, 1975, **94**, 65.
[7] H. Takahashi and J. Tsuji, *J. Organometallic Chem.*, 1967, **10**, 511.
[8] R. J. Cross and N. H. Tennent, *J. Organometallic Chem.*, 1973, **61**, 33.
[9] P. V. Roling, J. L. Dill, and M. D. Rausch, *J. Organometallic Chem.*, 1974, **68**, C33; P. V. Roling, D. D. Kirt, J. L. Dill, S. Hall, and C. Hallstrom, *ibid.*, 1976, **116**, 39.
[10] R. J. Cross and N. H. Tennent, *J. Organometallic Chem.*, 1974, **72**, 21.
[11] A. J. Cheney, W. S. McDonald, K. O'Flynn, B. L. Shaw, and B. L. Turtle, *J.C.S. Chem. Comm.*, 1973, 128.
[12] M. I. Bruce, B. L. Goodall, G. L. Sheppard, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 591.
[13] M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 558.

TABLE 1

Melting points and analytical data

Compound	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N	M [a,b]
(*i*) Azobenzenes, $XC_6H_4N{:}NPh$					
X = 2-F	30—32	71.5	4.5	13.9	200
		(72.0)	(4.5)	(14.0)	(200)
3-F	43—45	71.85	4.6	14.15	200
		(72.0)	(4.5)	(14.0)	(200)
4-F	83—84	71.6	4.4	13.9	200
		(72.0)	(4.5)	(14.0)	(200)
3-CF_3	30—32	62.4	3.5	11.4	250
		(62.4)	(3.6)	(11.2)	(250)
3-CO_2Et	Oil	71.0	5.65	11.0	254
		(70.9)	(5.5)	(11.0)	(254)
3-Me	Oil	79.85	6.4	14.8	196
		(79.6)	(6.1)	(14.3)	(196)
3-OMe	Oil	73.2	5.8	13.25	212
		(73.6)	(5.7)	(13.2)	(212)
(*ii*) Pentafluoroazobenzenes, $XC_6H_4N{:}NC_6F_5$					
X = 2-F	73—75	49.35	1.35	9.7	290
		(49.6)	(1.4)	(9.65)	(290)
3-F	57—58	49.1	1.35	9.75	290
		(49.6)	(1.4)	(9.65)	(290)
4-F	84—86	49.45	1.4	9.9	290
		(49.6)	(1.4)	(9.65)	(290)
3-CF_3	Oil	46.05	1.4	8.15	340
		(45.9)	(1.2)	(8.2)	(340)
3-Me	63—64	54.95	2.7	9.7	286
		(54.5)	(2.45)	(9.8)	(286)
(*iii*) Manganese complexes, $[Mn(N_2C_{12}H_8X)]$					
X = 2-F (11)	Oil	52.4	2.15	7.85	366
		(52.5)	(2.2)	(7.65)	(366)
3-F (9)	79—82	52.35	2.3	7.65	366
		(52.5)	(2.2)	(7.65)	(366)
4-F (13)	98—100	52.3	2.6	7.65	366
		(52.5)	(2.2)	(7.65)	(366)
3-CO_2Et (14)	38—40	54.5	3.25	6.65	420
		(54.3)	(3.1)	(6.7)	(420)
julolidine (30)	161—162	60.6	4.45	9.2	443
		(59.6)	(4.1)	(9.45)	(443)
julolidine (31)	130—133	60.1	4.3	9.8	443
		(59.6)	(4.1)	(9.45)	(443)
(*iv*) Manganese complexes, $[Mn(XC_6H_3N_2C_6F_5)(CO)_4]$					
X = 2-F (5)	83—84	42.4	0.6	6.2	456
		(42.2)	(0.65)	(6.15)	(456)
3-F (3)	58—60	42.3	0.75	6.2	456
		(42.2)	(0.65)	(6.15)	(456)
4-F (7)	67—69	42.15	0.75	6.15	456
		(42.2)	(0.65)	(6.15)	(456)
julolidine (32)	165—166	50.4	2.8	7.85	533
		(49.6)	(2.45)	(8.05)	(533)
(*v*) Palladium complexes, $[Pd(N_2C_{12}H_8X)(C_5H_5)]$					
X = 2-F (12)	35—37	55.8	3.55	7.5	370
		(55.2)	(3.5)	(7.6)	(370)
3-F (10)	85—87	55.4	3.5	7.5	370
		(55.2)	(3.5)	(7.6)	(370)
4-F (14)	93—95	55.7	3.6	7.4	370
		(55.2)	(3.5)	(7.6)	(370)
3-OMe (23)	118—120	56.65	4.1	7.5	382
		(56.6)	(4.2)	(7.35)	(382)
(*vi*) Palladium complexes, $[Pd(XC_6H_3N_2C_6F_5)(C_5H_5)]$					
X = 2-F (6)	155—157	43.9	1.4	6.5	460
		(44.4)	(1.7)	(6.1)	(460)
3-F (4)	133—135	44.2	1.8	5.7	460
		(44.4)	(1.7)	(6.1)	(460)
4-F (8)	154—156	44.8	2.1	5.9	460
		(44.4)	(1.7)	(6.1)	(460)

[a] Calculated values are given in parentheses. [b] By mass spectrometry.

RESULTS

Preparation of Substituted Azobenzenes.—A series of asymmetrically substituted azobenzenes was prepared by condensation of the appropriately substituted anilines with either nitrosobenzene or pentafluoronitrosobenzene in glacial acetic acid, followed by purification of the product by chromatography and recrystallisation.[14] The compounds $XC_6H_4N{:}NPh$ and $XC_6H_4N{:}NC_6F_5$ (X = 2-F, 3-F, 4-F, 3-CF_3, 3-CO_2Et, or 3-OMe) were so obtained. Analytical data are given in Table 1 and n.m.r. data in Table 2.

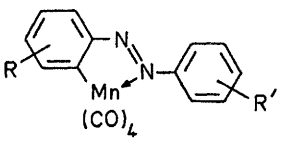
TABLE 2

N.m.r. data for substituted azobenzenes, $XC_6H_4N{:}N$(aryl)

Aryl	X	Chemical shifts * Aromatic protons	X	F_o	F_m	F_p
Ph	2-F	2.00—2.29 (m)	121.8			
C_6F_5	2-F	2.14—2.92 (m)	115.0	148.2	161.0	151.2
Ph	3-F	2.08—3.06 (m)	110.1			
C_6F_5	3-F	2.18—2.92 (m)	109.0	148.0	161.1	150.9
Ph	4-F	2.05—3.00 (m)	107.2			
C_6F_5	4-F	2.10 (d of d) (H^2, H^6), 2.87 (d of d) (H^3, H^5)	103.4	148.5	161.2	151.7
Ph	3-CF_3	1.95—3.05 (m)	62.3 (s)			
C_6F_5	3-CF_3	1.86—2.50 (m)	63.2 (s)	148.4	160.0	151.1
Ph	3-Me	2.14—2.90 (m)	7.68 (s)			
C_6F_5	3-Me	1.95—2.60 (m)	7.60 (s)	148.2	161.2	150.8
Ph	3-CO_2Et	1.70—2.96 (m)	5.40 (q), 8.65 (t)			
Ph	3-OMe	1.90—3.30 (m)	6.30 (s)			

* ^{1}H, in τ relative to internal $SiMe_4$ (τ 10.0); ^{19}F, in p.p.m. upfield from internal $CFCl_3$ (δ 0.0 p.p.m.).

Metallation Reactions.—Direct reaction of the substituted azobenzenes with $[MnMe(CO)_5]$ afforded the *ortho*-metallated tetracarbonylmanganese derivatives (1), which were readily characterised by the usual methods. Reactions with



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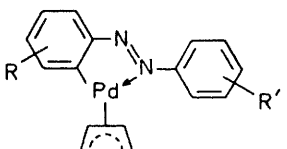


(2)

palladium(II) chloride gave insoluble and involatile chloride-bridged dimeric complexes, which were converted into the more readily characterised η-cyclopentadienyl complexes (2) by treatment with thallium(I) cyclopentadienide.

In most cases, the metallation reactions afforded a mixture of isomers of the product complexes (Table 3). Metallation of 2- or 4-X-substituted azobenzenes may give two possible isomers (Scheme), in which either the unsubstituted phenyl ring is metallated [isomer (a)] or the X-substituted ring is metallated, at position 6, with the X substituent *meta* to the metal atom [isomer (b)]. For 3-X-substituted azobenzenes three isomers are possible. Metallation of the unsubstituted Ph ring gives isomer (a), as above. If the X-substituted ring is metallated, the site of metallation may be either *ortho* or *para* to substituent X, giving isomers (b) or (c), respectively. The corresponding X-substituted pentafluoroazobenzenes afford only complexes in which the X-substituted ring has been metallated, and thus only one (2- or 4-X) or two (3-X) isomers are possible. These isomer counts assume: (*i*) free rotation of the non-metallated aromatic ring about the

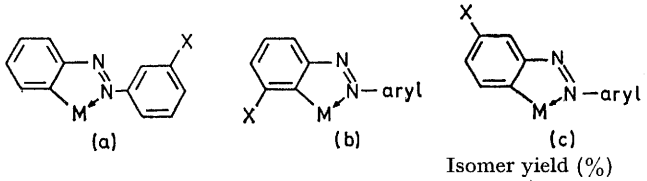
[14] Angeli and Valori, *Atti Accad. naz. Lincei*, 1913, **22**, I, 132 (*Chem. Abs.*, 1913, **7**, 2223); H. D. Anspon, *Org. Synth.*, 1955, Coll. vol. 3, 711.

C–N(azo) bond; (*ii*) metallation of the C_6F_5 ring does not occur; (*iii*) metallation does not occur by elimination of the substituent. The separation of the isomeric mixtures was very difficult, and for this reason our data have been collected using the pure complex isolated as an isomer mixture. We found no evidence that chromatography of the isomer mixture during purification procedures alters the ratios of products contained therein, as judged from n.m.r. spectra of the products before and after chromatography. The empirical composition of the complex was established by the usual methods (see Experimental section), while the configuration, ratio, and number of isomers in each case have been determined using ^1H and ^{19}F n.m.r. spectroscopy where appropriate.

TABLE 3

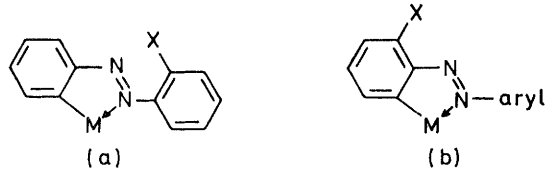
Products (and relative yields) obtained by metallation of mono-substituted azo- and pentafluoroazo-benzenes

3-Substituted



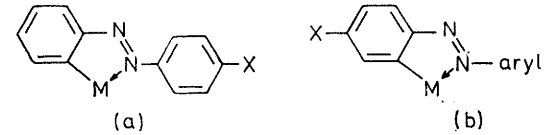
Complex	X	Aryl	M	Isomer yield (%) (a)	(b)	(c)
(3)	F	C_6F_5	$Mn(CO)_4$		100	
(4)	F	C_6F_5	$Pd(C_5H_5)$		*ca.* 1	*ca.* 99
(9)	F	Ph	$Mn(CO)_4$	20	80	
(10)	F	Ph	$Pd(C_5H_5)$	80	*ca.* 1	20
(15)	CF_3	C_6F_5	$Mn(CO)_4$			100
(16)	CF_3	Ph	$Mn(CO)_4$	50		50
(17)	CF_3	Ph	$Pd(C_5H_5)$	100		
(18)	Me	C_6F_5	$Mn(CO)_4$			100
(19)	Me	C_6F_5	$Pd(C_5H_5)$			100
(20)	Me	Ph	$Mn(CO)_4$	100		
(21)	Me	Ph	$Pd(C_5H_5)$	50		50
(22)	OMe	Ph	$Mn(CO)_4$	60	40	
(23)	OMe	Ph	$Pd(C_5H_5)$	10		90
(24)	CO_2Et	Ph	$Mn(CO)_4$		100	
(25)	CO_2Et	Ph	$Pd(C_5H_5)$		100	

2-Substituted



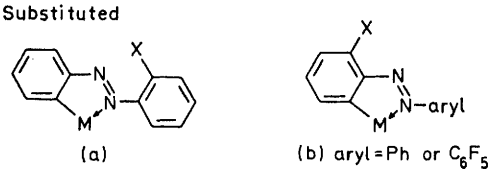
Complex	X	Aryl	M	Isomer yield (%) (a)	(b)
(5)	F	C_6F_5	$Mn(CO)_4$		100
(6)	F	C_6F_5	$Pd(C_5H_5)$		100
(11)	F	Ph	$Mn(CO)_4$	25	75
(12)	F	Ph	$Pd(C_5H_5)$	80	20

4-Substituted

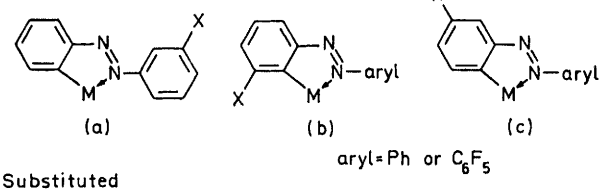


Complex	X	Aryl	M	Isomer yield (%) (a)	(b)
(7)	F	C_6F_5	$Mn(CO)_4$		100
(8)	F	C_6F_5	$Pd(C_5H_5)$		100
(13)	F	Ph	$Mn(CO)_4$	33	67
(14)	F	Ph	$Pd(C_5H_5)$	60	40

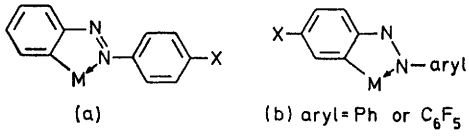
2 – Substituted



3 – Substituted



4 – Substituted



SCHEME Possible isomers of metallated monosubstituted azo- and pentafluoroazo-benzenes

(*a*) *Fluoroazobenzenes.* It is convenient to describe first the results we have obtained using the 3-fluoro-derivatives, since we have used some of the n.m.r. data to assign the structures of products formed in other reactions. The large chemical shifts associated with aromatic fluorines in different environments rendered the characterisation of the various isomers relatively easy. Initially, the complexes obtained from the pentafluorophenyl-substituted azo-compounds were studied.

The ^{19}F n.m.r. spectrum of the product from metallation of 3-$FC_6H_4N{:}NC_6F_5$ with $[MnMe(CO)_5]$ contains only one resonance (88.2 p.p.m.; apart from the usual 2 : 1 : 2 multiplets associated with the C_6F_5 group), indicating the presence of only one of the two possible isomers. In the free ligand, the F^3 resonance occurs at 109.0 p.p.m., and the large downfield shift found in the spectrum of the complex suggests that the fluorine is *ortho* to the σ-bonded $Mn(CO)_4$ group, *i.e.* structure (3b; X = F) (Table 3). This conclusion was verified by detailed analysis of the ^1H n.m.r. spectrum (Table 4). The signal at lowest field (τ 1.76) is assigned to H^6, being greatly deshielded by the neighbouring arylazo-group. The other two resonances arise from H^5 (τ 2.64, d of t) and H^4 (τ 2.88, d of d), both of which couple to the fluorine atom (8.0 and 5.5 Hz, respectively, *i.e. ortho* and *meta*). All the couplings have been confirmed by spin–spin decoupling experiments, and their magnitudes are within the ranges usually found for protons of this type.

The (η-cyclopentadienyl)palladium complex derived from this azobenzene also shows only one fluorine resonance (apart from the C_6F_5 signals), at 119.7 p.p.m. This upfield shift suggests that the complex has configuration (4c; X = F) (Table 3). Confirmation was again found in the ^1H n.m.r. spectrum (Table 4), where the signal at lowest field (τ 2.12) is assigned to H^6, *ortho* to the arylazo-group. Assignment of the other two signals in the aromatic region to H^3 and H^4 resulted from analysis of the coupling constants. In this case, the fluorine atom shows two *ortho*-couplings to H^4 and H^6, both of 9.0 Hz.

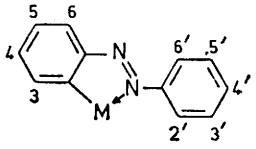
Using 2-$FC_6H_4N{:}NC_6F_5$, metallation with manganese or palladium afforded only one isomer, characterised as (5) and (6), respectively, from their n.m.r. spectra. The fluorine atom (C_6H_4F) resonated at 106.4 and 105.9 p.p.m. respectively, a downfield shift compared with the resonance in the free ligand, which occurs at 115 p.p.m. With 4-$FC_6H_4N{:}NC_6F_5$ only one isomer is possible if the *ortho*-C–H bond is attacked, and the complexes formed were identified as [(7); M = $Mn(CO)_4$] or [(8); M = $Pd(\eta\text{-}C_5H_5)$]. In these cases the resonance of the fluorine atoms is shifted only slightly upfield from that in the free ligand.

Identification of the isomers formed by *ortho*-metallation of the three monofluoroazobenzenes $FC_6H_4N{:}NPh$ was more difficult, because the aromatic region of the ^1H n.m.r. spectra contained Ph resonances as well as the ones used to confirm the above structure assignments for the C_6F_5 derivatives. Assuming free rotation of the C_6H_4X group in complexes containing a metallated Ph ring, three isomers were possible. This suggested that the aromatic region of the ^1H n.m.r. spectra would give little structural information. However, the ^{19}F n.m.r. spectra were most useful in this regard, and consideration of the chemical shifts and

TABLE 4

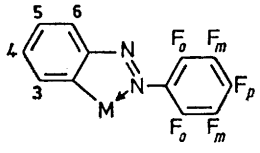
N.m.r. data for metallated azobenzene complexes [a]

(*a*) Complexes of type $M(N_2C_{12}H_8X)$



Complex	X	M	N.m.r. data: X	Aromatic protons	η-C_5H_5
(9a)	3′-F	$Mn(CO)_4$	108.7	1.82—3.16	
(9b)	3-F	$Mn(CO)_4$	86.3		
(10a)	3′-F	$Pd(C_5H_5)$	109.8	1.84—3.52	4.31 (br)
(10b)	3-F	$Pd(C_5H_5)$	90.5		
(10c)	5-F	$Pd(C_5H_5)$	117.4		
(11a)	2′-F	$Mn(CO)_4$	118.2	1.76—3.10	
(11b)	6-F	$Mn(CO)_4$	110.0		
(12a)	2′-F	$Pd(C_5H_5)$	121.4	1.82—3.40	4.30
(12b)	6-F	$Pd(C_5H_5)$	108.5		4.34
(13a)	4′-F	$Mn(CO)_4$	108.1	1.66—3.20	
(13b)	4-F	$Mn(CO)_4$	102.9		
(14a)	4′-F	$Pd(C_5H_5)$	108.7	1.84—3.36	4.32
(14b)	4-F	$Pd(C_5H_5)$	109.6		4.34
(16a)	3′-CF_3	$Mn(CO)_4$	62.37, 62.78	1.86—3.12	
(16c)	5-CF_3	$Mn(CO)_4$			
(17a)	3′-CF_3	$Pd(C_5H_5)$	62.24	1.76—3.30	4.14
(20a)	3′-Me	$Mn(CO)_4$	7.6	1.96—2.94	
(21a)	3′-Me	$Pd(C_5H_5)$	7.65, 7.7	1.90—3.52	4.32
(21c)	5-Me	$Pd(C_5H_5)$			
(22a)	3′-OMe	$Mn(CO)_4$	6.19	1.70—3.36	
(22b)	3-OMe	$Mn(CO)_4$	6.16		
(23a)	3′-OMe	$Pd(C_5H_5)$	6.28	1.88—3.62	4.28
(23c)	5-OMe	$Pd(C_5H_5)$	6.20		
(24b)	3-CO_2Et	$Mn(CO)_4$	5.75 (q), 8.50 (t)	1.98—2.90	
(25b)	3-CO_2Et	$Pd(C_5H_5)$	5.68 (q), 8.60 (t)	1.40—3.40	4.14

(*b*) Complexes of type $M(XC_6H_3N_2C_6F_5)$ [b]

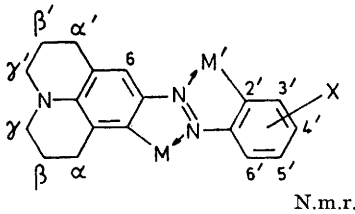


Complex	X	M	N.m.r. data: H^3	H^4	H^5	H^6	F_o	F_m	F_p	η-C_5H_5
(3b)	3-F	$Mn(CO)_4$	*88.2*	2.88 (d of d)	2.64 (d of t)	1.76 (d)	150.5	161.0	154.3	
(4c) [c]	5-F	$Pd(C_5H_5)$	2.17 (d of d)	3.33 (d of t)	*119.7*	2.12 (d of d)	150.5	162.8	156.8	4.33 (s)
(5b)	6-F	$Mn(CO)_4$	2.11 (d)	2.53 (d of t)	3.06 (d of d)	*106.4*	148.9	158.3	152.3	
(6b)	6-F	$Pd(C_5H_5)$	2.38 (d of d)	3.12 (d of t)	3.32 (d of t)	*105.9*	147.6	160.6	153.0	4.34 (s)
(7b)	4-F	$Mn(CO)_4$	2.18 (d of d)	*100.0*	2.97 (d of t)	1.60 (d of d)	149.6	159.5	152.2	
(8b)	4-F	$Pd(C_5H_5)$	2.51 (d of d)	*107.4*	3.19 (d of t)	1.82 (d of d)	147.7	160.5	154.2	4.37 (s)
(15c)	5-CF_3	$Mn(CO)_4$	1.68 (d)	2.44 (d of d)	*62.9* (s)	1.41 (d)	149.2	158.8	152.1	
(18c)	5-Me	$Mn(CO)_4$	1.99d	2.78 (d of d)	*7.58* (s)	1.81 (d)	149.7	160.3	153.0	
(19c)	5-Me	$Pd(C_5H_5)$	2.27d	3.34 (d of d)	*7.66* (s)	2.00 (d)	149.1	160.4	153.5	4.38 (s)

Coupling constants (Hz): (3b), $J(H^4H^5)$ 7.5, $J(H^4F)$ 8.0, $J(H^5H^6)$ 7.5, $J(H^4H^6)$ 0; (4c), $J(H^3H^4)$ 9.0, $J(H^3F)$ 6.0, $J(H^4H^6)$ 3.0, $J(H^4F)$ 9.0, $J(H^6F)$ 9.0; (5b), $J(H^3H^4)$ 8.0, $J(H^4H^5)$ 8.0, $J(H^4F)$ 4.5, $J(H^5F)$ 9.0, $J(H^3H^5)$ 0; (6b), $J(H^3H^4)$ 7.5, $J(H^4H^5)$ 7.5, $J(H^4F)$ 5.0, $J(H^5F)$ 7.5, $J(H^3H^5)$ 1.0; (7b), $J(H^3H^5)$ 2.5, $J(H^3F)$ 8.0, $J(H^5H^6)$ 8.5, $J(H^5F)$ 8.5, $J(H^6F)$ 5.0; (8b), $J(H^3H^5)$ 2.5, $J(H^3F)$ 8.0, $J(H^5H^6)$ 8.5, $J(H^5F)$ 8.5, $J(H^6F)$ 5.0; (15c), $J(H^3H^4)$ 8.0, $J(H^4H^6)$ 1.0; (18c), $J(H^3H^4)$ 8.0, $J(H^4H^6)$ 2.0; (19c), $J(H^3H^4)$ 7.0, $J(H^4H^6)$ 1.0.

TABLE 4 (*Continued*)

(*c*) Azojulolidine complexes



Complex	M	M′	X	N.m.r. data: H_α	$H_{\alpha\alpha'}$	$H_{\alpha'}$	$H_{\beta\beta'}$	$H_{\gamma\gamma'}$	H^2	H^6	Ph	F_o	F_m	F_p
(28)	H	H	H		7.26 (t)		8.04 (d of t)	6.76 (t)		2.28—2.84 (m)				
(30)	H	$Mn(CO)_4$	H		7.12 (t)		8.10 (d of t)	6.72 (t)		1.96—2.14 (m)				
(31)	$Mn(CO)_4$	H	H	7.12 (t)		7.04 (t)	7.98 (d of t)	6.60 (q)	2.52 (s)	2.66 (m)	2.80—2.92 (m)			
(29)	H	H	F		7.12 (t)		8.00 (d of t)	6.66 (t)		2.71 (s)		148.1	159.5	154.0
(32)	$Mn(CO)_4$	F	F	7.00 (t)		7.20 (t)	7.92 (m)	6.54 (q)		2.46 (s)		150.5	163.0	158.8

[a] All the spectra are for solutions in CS_2. Chemical shifts in τ (^1H, relative to internal $SiMe_4$ at τ 10.0) or p.p.m. upfield from internal $CFCl_3$ (^{19}F: δ 0.0 p.p.m.). [b] Chemical shifts of substituents are given in italics. [c] Showed weak signal at 91.0 p.p.m. (F^3).

relative intensities of the resonances enabled an unequivocal assignment of structures to be made.

The product obtained on manganation of 3-fluoroazobenzene contained two isomers, as evidenced by two fluorine resonances at 86.3 and 108.7 p.p.m. (*cf.* the azobenzene at 110.1 p.p.m.), with relative intensity 4 : 1, respectively. The more intense lower-field signal is assigned to isomer (9b), and exhibits the usual deshielding found with a transition-metal group *ortho* to fluorine. On the basis of the similarity of chemical shift with that of the free ligand, the second isomer is assigned structure (9a), and is formed by metallation of the unsubstituted Ph group. The third possible isomer would be expected to show a fluorine resonance upfield from that found in the free ligand. Palladation of this fluoroazobenzene affords a mixture of three isomers, giving three fluorine resonances, and three close cyclopentadienyl resonances (Table 4). These are readily assigned to the three possible isomers (10a, b, and c, respectively), formed in a *ca.* 80 : 1 : 20 ratio, based on the relative intensities of the n.m.r. resonances.

The ^{19}F chemical shifts of 2- and 4-fluoroazobenzenes are 121.8 and 107.2 p.p.m. respectively (Table 2). Manganation and palladation of the 2-isomer afforded a mixture of two complexes in each case (Table 3). The ^{19}F n.m.r. spectrum (Table 4) of the former exhibited two signals at 110.0 and 118.2 p.p.m., while the palladium complexes showed signals at 108.5 and 121.4 p.p.m. The latter also show two cyclopentadienyl resonances. The ^{19}F signals at higher field are assigned to complexes containing the azobenzene metallated in the Ph ring, (11a) and (12a), while the other signals are assigned to the isomer in which the fluorine-substituted ring is metallated, (11b) and (12b). These are the only two isomers possible in this case. If metallation occurred by fluorine abstraction in either case, the known complexes $[Mn(CO)_4L]$ or $[Pd(C_5H_5)L]$ (HL = azobenzene) would have been formed, but no evidence for their formation was found. Similarly metallation of the 4-isomer afforded two isomers in each case, with ^{19}F n.m.r. resonances at 103 and 108 (Mn) or 109 and 110 p.p.m. (Pd) (Table 4). Those at *ca.* 109 p.p.m. are readily assigned to complexes in which the C_6H_5 ring has been metallated, (13a) and (14a), while the other resonances arise from the other possible isomer, (13b) and (14b). The difference in chemical shift on replacing the $Mn(CO)_4$ group by $Pd(C_5H_5)$ is noteworthy.

(*b*) *Azobenzenes bearing other substituents.* Having identified the various isomers from their ^{19}F n.m.r. spectra, it was then possible to return to the ^1H n.m.r. spectra, and to assign the various signals on the basis of their relative intensities, and also the data obtained using the pentafluorophenyl-substituted complexes. The various assignments are listed in Table 4.

The reaction between $[MnMe(CO)_5]$ and $3\text{-}F_3CC_6H_4N{:}NC_6F_5$ afforded only one of the two possible isomers, as shown by the presence of only one CF_3 resonance in the ^{19}F n.m.r. spectrum. Analysis of the ^1H n.m.r. spectrum (Table 4) enabled the structure to be assigned as (15c) (Table 3). In contrast, we were unable to effect metallation of this azobenzene using $PdCl_2$. Using $3\text{-}F_3CC_6H_4N{:}NPh$, manganation afforded complexes (16a) and (16c) in equal amounts, the assignments being based on the ^1H n.m.r. spectra and comparisons with the analogous 3-F complexes. Palladation afforded one complex, (17a), in which the C_6H_5 ring had been metallated. Metallation of $3\text{-}MeC_6H_4N{:}NC_6F_5$ afforded only one complex in each case, (18c) and (19c), shown to be the isomer in which the methyl group is *para* to the metal atom. The formation of this isomer was indicated by the ^1H n.m.r. spectra with a methyl resonance at τ 7.6 (Mn) or 7.7 (Pd), and coupling constants showing one *ortho*- and one *meta*-hydrogen. The non-fluorinated azobenzene reacted to give only (20a) with $[MnMe(CO)_5]$, while equal amounts of (21a) and (21b) were formed using $PdCl_2$. Reaction at the C_6H_5 ring was indicated by the constant chemical shift of the methyl group [τ 7.6 (Mn) and 7.65 (Pd), *cf.* free ligand at τ 7.7], while the second palladated complex had a signal at τ 7.7, which may be compared to the fluorinated complex at τ 7.6.

The reactions with methoxy- and ethoxycarbonyl-substituted azobenzenes were only carried out with the non-fluorinated derivatives. Manganation of $3\text{-}MeOC_6H_4N{:}NPh$ afforded the two isomers (22a) and (22b) in 3 : 2 proportion, whereas palladation gave a 1 : 9 ratio of (23a) and (23c). The composition of these isomeric mixtures could not be directly determined from the ^1H n.m.r. spectra, as a result of the large number of aromatic protons and the consequent complexity of the spectra. However, the differing proportions enabled the complexes to be rationalised according to the above results, and assignments of the aromatic resonances are consistent with our interpretation. Reactions of $3\text{-}EtO_2CC_6H_4N{:}NPh$ gave only one complex in each case, shown to be the same positional isomer, in which metallation had occurred in the substituted ring, *ortho* to both the CO_2Et and azo-functions, (24b) and (25b).

DISCUSSION

Metallation of a substituted azobenzene may proceed to give several possible isomeric products. In the present work, we have assumed that the products of type $[Mn(CO)_4L]$ or $[Pd(C_5H_5)L]$ contain a five-membered ring formed by *ortho*-metallation of the aromatic ring distant from the co-ordinated nitrogen atom, similar to the chelate rings found in $[Mn(C_6H_4CH{:}NPh)(CO)_4]$ [15] or $[\{PtCl(C_6H_4N{:}NPh)\}_2]$.[16] Further, we have found no evidence for metallation by attack on the C_6F_5 group (where present), and thus metallation must have occurred by loss of the *ortho*-hydrogen as methane {from $[MnMe(CO)_5]$} or HCl (from $PdCl_2$). With these restrictions, and the assumption of free rotation of the non-metallated ring about the C–N bond, the possible isomers that may be found are summarised in the Scheme. In the examples containing a C_6F_5 group, isomer (a) cannot be formed.

Consideration of the results obtained for the fluorinated azobenzenes shows that manganation occurs on the substituted ring, whereas palladation of the unsubstituted ring occurs. Where there is no unsubstituted ring, palladation occurs at the least deactivated position (if a choice is available), to give only isomer (c). This can be simply explained if we consider the effect of the fluorine substituent which, as a powerfully electron-attracting group, would tend to withdraw electron density from positions *ortho* to it. The *meta*-position would be relatively little affected. At the same time we must also consider the effect of the arylazo-group, itself strongly electron withdrawing. In the 3-fluoro-isomer the combined effect is to make position 2 highly electron deficient, with position 6 less so. The least electropositive of the *ortho* positions is 2′ on the unsubstituted ring, or 6 for the C_6F_5 derivatives. That manganation and palladation proceed to give high yields of isomers (a) and (b) respectively is a striking demonstration of the differing electronic characters of the two reagents used.

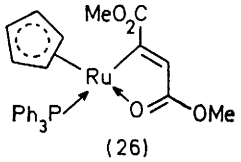
The results obtained with the 2- and 4-isomers support the general conclusions that palladation occurs in the ring with the most electron density, as previously found for 4-dimethylaminoazobenzene,[7] and manganation occurs at the ring with least electron density.

Similarly, we have shown that substitution of the trifluoromethyl-substituted compounds gives products consistent with the above interpretation. In this case, reaction of $[MnMe(CO)_5]$ at the more favoured 2-position may be prevented by steric interaction with the bulky CF_3 group. It is notable that 3-$F_3CC_6H_4N{:}NC_6F_5$ is not palladated, both possible metallation positions being totally deactivated towards electrophilic attack by the extremely powerful inductive effect of the CF_3 group. Palladation of 3-$F_3CC_6H_4N{:}NPh$ occurs exclusively in the Ph group.

Use of electron-donating substituents resulted in a different pattern of substitution. Palladation of 3-$MeC_6H_4N{:}NC_6F_5$ gave the same isomer as manganation, although the latter reaction was unusually slow, with considerable decomposition occurring. In this case, the 6-position is expected to be highly activated toward electrophilic attack by the *p*-CH_3 group. That metallation did not occur at the 2-position can probably be attributed to the steric effect of the methyl group. The 6-position would be activated toward nucleophilic attack by the arylazo-group. In the case of 3-$MeC_6H_4N{:}NPh$, manganation occurs exclusively in the Ph group rather than the strongly deactivated tolyl ring. In contrast, palladation of both rings occurs to approximately the same extent.

Identification of the isomers found with 3-$MeOC_6H_4N{:}NPh$ was made using the results mentioned above. Thus, palladation afforded two isomers in a 1 : 9 ratio, to which structures (23a) and (23c) were assigned. The high yield of (23c) can be explained by activation of the 6-position by the strongly *para*-directing mesomeric effect of the methoxy-group. The formation of two isomers in the manganation reaction results from attack on the unsubstituted ring, and by attack at the 2-position of the C_6H_4OMe group, activated towards nucleophilic attack by the electron-withdrawing inductive effects of the adjacent methoxy- and arylazo-groups.

Other factors may also affect the position of metallation. Using the simple criteria of the electronic properties of the substituent would lead to the prediction that manganation and palladation of 3-ethoxycarbonylazobenzene would afford isomers (24a) and (24c), and (25a), respectively. In fact, the reactions of this azo-compound with $[MnMe(CO)_5]$ gave (24b), while $PdCl_2$ reacted to give (25b). These unexpected results might be explained by assuming an intermediate in which the CO_2Et group interacts with the incoming metal atom, thus forcing the observed stereochemistry on the metallated complex. A growing number of complexes containing an ester carbonyl group co-ordinated to a metal atom *via* an oxygen–metal σ-donor



(26)

bond are known, including complex (26), formed by displacement of PPh_3 by the ester carbonyl function.[17]

Our results are explicable in broad terms by the simple idea that manganation occurs at the most electron-deficient carbon atom, and palladation occurs at the most electron-rich carbon atom, reactions which can be described as *nucleophilic* and *electrophilic*, respectively. Further examination of the product ratios found in reactions of azobenzenes containing a Ph

[15] R. G. Little and R. J. Doedens, *Inorg. Chem.*, 1973, **12**, 840.
[16] R. C. Elder, R. D. Cruea, and R. F. Morrison, *Inorg. Chem.*, 1976, **15**, 1623.
[17] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

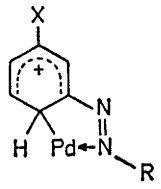
group indicates that some metallation of the group occurs even when it appears that the most favoured position of attack is in the substituted ring.

This observation can be explained by considering the overall course of these reactions. For example, the initial product of the reaction between azobenzene and $PdCl_2$ is the *N*-donor complex, $[PdCl_2(HL)_2]$ (HL = azobenzene),[18] whose structure has recently been confirmed by an *X*-ray study.[19] Subsequent heating of this material affords the *ortho*-metallated product originally obtained by Cope and Siekman.[20] We have not been able to observe the formation of a similar *N*-bonded complex of manganese, but it is reasonable to suppose that the first step in all these reactions is co-ordination of one of the azo-nitrogen atoms to the metal centre. The relative electron-donor power of these atoms in the azo-function should be affected only slightly by the presence of a 3 substituent, and so *either* nitrogen atom could co-ordinate. The subsequent position of metallation is then a function of the degree of activation of the carbon atom metallated, the product ratio reflecting these competitive reactions. In the case of the C_6F_5 compounds the fluorinated ring is not metallated, and the initial *N*-bonded intermediate may decompose, perhaps by migration of the metal group to the other nitrogen atom.

We have discussed previously the possible course of the metallation reaction using alkylmanganese complexes, and have pointed out that a concerted reaction involving nitrogen co-ordination and alkyl migration is probably involved.[6] Certainly the failure to detect any non-metallated *N*-bonded intermediate supports this suggestion. We [21] and other workers [22] have also shown that it is possible to obtain bis(*ortho*-metallated) derivatives in which both nitrogen atoms are involved, suggesting that the donor power of the non-co-ordinated nitrogen atom is little affected by the other, co-ordinated, atom. In the present work, we obtained no evidence for the formation of similar disubstituted complexes.

Parshall [3,23] has suggested that the initial attack of Pd^{II} on an aromatic substrate may involve co-ordination to the face of the aromatic ring. With azobenzenes, co-ordination by nitrogen probably positions the metal atom to generate the C–Pd bond *via* an intermediate such as (27). Such a *para*-intermediate, which would be preferentially stabilised, would explain the predominance of isomer (c) in the products of the palladation reactions.

Conclusions.—In summary, therefore, the results of the present study are accounted for by the proposals that: (*i*) metallation is preceded by initial co-ordination of either of the two azo-nitrogen atoms; (*ii*) the presence of the electron-withdrawing arylazo-function in each ring activates both rings towards nucleophilic attack; (*iii*) the favoured site of metallation is determined by the nature of the substituent on the ring, *electron-withdrawing* substituents (F or CF_3) activating the ring



(27)

to attack by *nucleophilic* reagents (*e.g.* low-valent metal complexes), while *electron-donating* substituents (Me or OMe) activate the ring towards *electrophilic* attack (*e.g.* $PdCl_2$); (*iv*) some substituents (CO_2Et) may alter the course of reaction by virtue of an interaction with the metal reagent which predominates over the electronic considerations mentioned above.

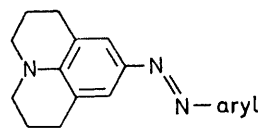
This investigation has given some insight into some of the electronic factors influencing cyclometallation reactions. Other factors besides the nature of the metal-containing group are also important: the nature of the C–H bond itself determines the ease of cleavage, which is already known to decrease in the order: aromatic > olefinic > aliphatic. Shaw [24] has also demonstrated that steric factors influence the metallation of tertiary phosphines and arsines, and a recent study using both experiment and theory has emphasised the interplay of these several factors in determining whether reaction of a particular C–H bond will take place.[25] As has been pointed out previously,[2,23] the cyclometallation reaction is but one aspect of the general problem of the activation of C–H bonds, and many problems remain to be resolved.

Azojulolidine complexes. In the early stages of this work, we were anxious to use azobenzene derivatives containing suitable substituents which would simplify the ^1H n.m.r. spectra. Accordingly, we examined the manganation of the dyestuffs phenylazojulolidine (28; aryl = Ph) and pentafluorophenylazojulolidine * (29; aryl = C_6F_5).[26] From the former reaction two isomeric complexes were obtained, which were readily separated by chromatography, in contrast to the isomer mixtures discussed in the earlier part of this paper. This ease of separation is probably a result of the relatively large size of the fused-ring part of the azojulolidine nucleus. The parent azo-compounds are intensely coloured, and the two isomers were (in order of elution from the column) deep purple (30) and deep red (31) solids. The latter was readily identified from its ^1H n.m.r. spectrum

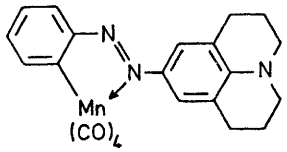
* Julolidine = 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine.

[18] A. L. Balch and D. Petridis, *Inorg. Chem.*, 1969, **8**, 2247; R. Murray, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 811.
[19] G. P. Khare, R. G. Little, J. T. Veale, and R. J. Doedens, *Inorg. Chem.*, 1975, **14**, 2475.
[20] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.
[21] R. L. Bennett, M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *Austral. J. Chem.*, 1974, **27**, 2131.
[22] I. V. Barinov, T. L. Voevodskaya, and Y. A. Ustynyuk, *J. Organometallic Chem.*, 1971, **30**, C28.
[23] G. W. Parshall, 'Catalysis,' *Specialist Periodic Report*, The Chemical Society, London, 1977, p. 335.
[24] B. L. Shaw, *J. Amer. Chem. Soc.*, 1975, **97**, 3856.
[25] J. F. van Baar, K. Vrieze, and D. J. Stufkens, *J. Organometallic Chem.*, 1975, **97**, 461.
[26] R. W. Castelino and G. Hallas, *J. Chem. Soc.* (*B*), 1971, 793.

which contained a singlet at τ 2.52, assigned to the lone aromatic proton on the polycyclic nucleus, as well as the usual broad phenyl resonance at τ 2.66, as the isomer in which the polycyclic nucleus was substituted, while the first complex eluted was the isomer containing



(28) aryl = Ph
(29) aryl = C_6F_5



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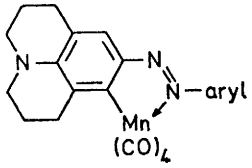

(31) aryl = Ph
(32) aryl = C_6F_5

a metallated phenyl ring. In the case of (29; aryl = C_6F_5), only one complex was obtained, as a deep red solid, and readily characterised as (32). As with the non-fluorinated compound, a singlet in the aromatic region at τ 2.46 was characteristic.

EXPERIMENTAL

All the reactions were carried out under nitrogen, although no special precautions were taken to exclude oxygen during work-up. Spectra were obtained with Perkin-Elmer 457 (i.r.), Varian Associates HA 100 (^{1}H n.m.r. at 100 MHz, ^{19}F n.m.r. at 94.1 MHz), or A.E.I.-G.E.C. MS 902 instruments (mass, at 70 eV * ionising energy). Materials were purified by methods described in previous Parts of this Series. Chromatography was on columns of Florisil. Analyses are collected in Table 1; complexes (15)—(22) and (25) were identified only spectroscopically (*i.e.* from their n.m.r. and mass spectra; all the complexes showed the appropriate molecular ion). N.m.r. data for substituted azobenzenes are in Table 2, while those for the metallated complexes are in Table 4; Table 5 lists ν(CO) bands for the $Mn(CO)_4$ derivatives.

Synthesis of Azobenzenes.—(*i*) $XC_6H_4N{:}NPh$. A mixture of nitrosobenzene (10 mmol) and an excess of the appropriately substituted aniline, $XC_6H_4NH_2$ (12 mmol), was stirred in glacial acetic acid (30 cm^3) at room temperature for 2 h. The resulting brown solution was neutralised with sodium hydrogencarbonate, and extracted with diethyl ether to give an orange solution. Reduction in volume was followed by chromatography on Florisil, elution with light petroleum affording the azobenzene (60—80%).

(*ii*) $XC_6H_4N{:}NC_6F_5$. Similar reactions using pentafluoronitrosobenzene (2.5 mmol, Bristol Organics Ltd.) and the appropriately substituted aniline (3.0 mmol) afforded the corresponding pentafluoroazobenzenes (40—50%).

* Throughout this paper: 1 eV $\approx$ 1.60 $\times$ 10^{-19} J.

Preparation of Manganese Complexes.—(*a*) A mixture of [$MnMe(CO)_5$] (1.0 mmol) and the azobenzene (1.0 mmol) was heated in refluxing light petroleum (40 cm^3) for 3 h. Chromatography of the concentrated solution on Florisil gave a red band (eluted with light petroleum–diethyl ether) which on evaporation and recrystallisation afforded the metallated complex (50—90%).

TABLE 5

Carbonyl-stretching bands (cm^{-1}) for solutions in cyclohexane

Complex	Aryl	X	ν(CO)
(3)	C_6F_5	3-F	2 094m, 2 021vs, 2 018 (sh), 1 977s
(5)	C_6F_5	2-F	2 093m, 2 018vs, 2 009ms, 1 971s
(7)	C_6F_5	4-F	2 095m, 2 018vs, 2 009s, 1 972vs
(9)	Ph	3-F	2 084m, 2 006vs, 1 999s, 1 963s
(11)	Ph	2-F	2 083m, 2 005vs, 1 998s, 1 962s
(13)	Ph	4-F	2 085m, 1 996vs, 1 992 (sh), 1 964s
(15)	C_6F_5	3-CF_3	2 088s, 2 014s, 2 006s, 1 968s
(16)	Ph	3-CF_3	2 083m, 2 006s, 2 004 (sh), 1 964s
(18)	C_6F_5	3-Me	2 084m, 2 010s, 2 000s, 1 963s
(20)	Ph	3-Me	2 080m, 2 000vs, 1 994 (sh), 1 956s
(22)	Ph	3-OMe	2 081m, 2 002vs, 1 997 (sh), 1 959s
(24)	Ph	3-CO_2Et	2 083m, 2 006vs, 2 002 (sh), 1 964s, 1 730m

(*b*) A mixture of [$MnMe(CO)_5$] (100 mg, 0.48 mmol) and azojulolidine (100 mg, 0.36 mmol) was heated in refluxing light petroleum (50 cm^3) for 1.5 h. After removal of solvent, chromatography afforded a deep purple band (eluted with benzene) which gave magenta crystals of complex (30) (52 mg, 33%), and an intense magenta band (eluted with diethyl ether) which afforded deep red crystals of complex (31) (103 mg, 64%).

(*c*) A similar reaction using [$MnMe(CO)_5$] (35 mg, 0.17 mmol) and pentafluoroazojulolidine (50 mg, 0.13 mmol) gave deep red crystals of complex (32) (48 mg, 69%).

Preparation of Palladium Complexes.—The azobenzene (2.0 mmol) was added to a suspension of palladium(II) chloride (2.0 mmol) in methanol (40 cm^3), and the mixture was stirred at room temperature for 3 h. The resulting orange-red precipitate of the dimeric chloropalladium derivative (*ca.* 90%) was filtered off and washed with methanol and diethyl ether. Alternatively, a clear brown solution of $Li_2[PdCl_4]$, obtained by adding 2 mol. equivalents of LiCl to a suspension of $PdCl_2$ in methanol, was treated with the azobenzene to give the same products. The (η-cyclopentadienyl)palladium complexes were obtained by addition of excess of thallium(I) cyclopentadienide (4.0 mmol) to the appropriate chloropalladium complex (1.5 mmol) in tetrahydrofuran (40 cm^3), followed by refluxing for 1 h. Filtration, reduction in volume, and chromatography afforded the dark blue products (80–95%), which were eluted with light petroleum–diethyl ether.

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