Cyclometallation Reactions. Part 10.[1] Some Reactions of Polyfluorinated Azobenzenes: Metallation by Fluorine Abstraction

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The reactions of 2,3,4,5,6-pentafluoroazobenzene and 2*H*-nonafluoroazobenzene with a variety of transition-metal complexes have been examined. In one case, metallation by abstraction of fluorine occurs, in addition to the usual metallation reactions found with azobenzene. The ^{1}H and ^{19}F n.m.r. spectra are discussed.

THE formation, directly from azobenzenes, of chelated 2-(phenylazo)phenyl derivatives of transition metals involves elimination of the aryl hydrogen. Combination with a suitable leaving group on the metal results in the formation of small molecules, such as H_2 (or metal hydride), HCl, CH_4, or C_5H_6.[2] We have recently described[3] reactions in which attack on an electron-deficient centre by a low-valent metal complex occurs. The chemistry of polyfluoroaromatic compounds is dominated by their reactivity towards nucleophiles; reactions with carbonylmetal anions to give metal–carbon σ-bonded species, for example, are well-documented.[4]

As part of our studies of the *ortho*-metallation phenomenon, we have examined the reactions between several polyfluorinated derivatives of azobenzene and a variety of transition-metal complexes. We were interested to determine whether, in a molecule such as 2,3,4,5,6-pentafluoroazobenzene $C_6F_5N{=}NC_6H_5$, the expected metallation of the C_6H_5 ring would be accompanied by any products resulting from nucleophilic attack on the fluoroaromatic group. Some of the resulting complexes have also provided the opportunity for a better assignment of the proton resonances in the metallated ring.

Preparation of Fluorinated Azobenzenes.—2,3,4,5,6-Pentafluoroazobenzene (I) was prepared by condensation of pentafluoronitrosobenzene with aniline in glacial acetic acid.[5] Tar formation in the slightly exothermic reaction was reduced by carrying out the reaction at 0 °C. The product was finally isolated as orange needles in up to 80% yield by chromatography. 2*H*-Nonafluoroazobenzene (II) was obtained in a much lower yield (15%), using 2,3,4,5-tetrafluoroaniline. Finally, reaction of (I) with sodium methoxide gave the 4-methoxytetrafluoro-compound (III) as a bright orange solid.

These compounds were characterised by analysis (Table 1) and spectroscopic methods. The i.r. spectra contain bands arising from the fluorinated aromatic ring at 1640m and 1500vs cm^{-1}, in addition to the usual strong CF absorptions between 1000 and 1400 cm^{-1}, while the C_6H_5 group gives rise to bands around 730 cm^{-1}, together with a ring vibration at *ca.* 1520 cm^{-1}. The mass spectra contained characteristic ions resulting from all possible cleavages of the C–N and N–N bonds. Other ions in the spectra were consistent with the usual fragmentation pathways followed by azo-compounds[6] and polyfluoroaromatics.[7] The ^{1}H n.m.r. spectra (Table 2) contained resonances in the aromatic region (τ *ca.* 2·1 and 2·6), together with a peak at τ 5·91 for the methyl group in (III). The ^{19}F n.m.r. spectra (Table 2) of the pentafluorophenyl compounds contained the expected

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[1] Part 9, M. I. Bruce, B. L. Goodall, F. G. A. Stone, and B. J. Thomson, *Austral. J. Chem.*, 1974, **27**, 2135.

[2] M. I. Bruce and B. L. Goodall, in S. Patai, ed., 'The Chemistry of Hydrazo, Azo and Azoxy Groups,' John Wiley, New York, ch. 9, p. 259.

[3] M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 558.

[4] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, 1968, **80**, 835; *Internat. Edn.*, 1968, **7**, 747.

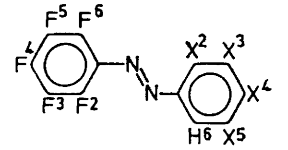
[5] R. B. Wagner and H. D. Zook, 'Synthetic Organic Chemistry,' John Wiley, New York, 1953, p. 765.

[6] J. H. Bowie, G. E. Lewis, and R. G. Cooks, *J. Chem. Soc.* (*B*), 1967, 621.

[7] L. D. Smithson, A. K. Bhattacharya, and C. Tamborski, *Org. Mass Spectrometry*, 1970, **4**, 1.

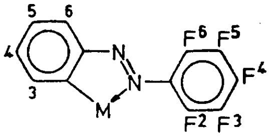
2 : 1 : 2 pattern of resonances, while a simpler spectrum was obtained for (III), with only two AA′XX′ resonances being observed.

Reactions of Polyfluoro Azo-compounds.—(i) *With manganese and rhenium complexes.* The reaction between $[Mn(CO)_5Me]$ and (I) proceeded readily to give the expected complex, $[C_6F_5N{=}NC_6H_4Mn(CO)_4]$ (IV), together with a bright yellow, light-sensitive, material initially exhibiting three ν(CO) bands at 2014, 1944, and 1924 cm^{-1}, but rapidly decomposing to a ketonic product [ν(CO) 1714 cm^{-1}], which was not further characterised.



(I) X^{2-5} = H

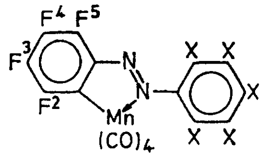
(II) X^{2-5} = F



(IV) M = Mn(CO)$_4$

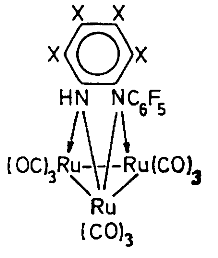
(VII) M = Re(CO)$_4$

(XI) M = Pd(C_5H_5)



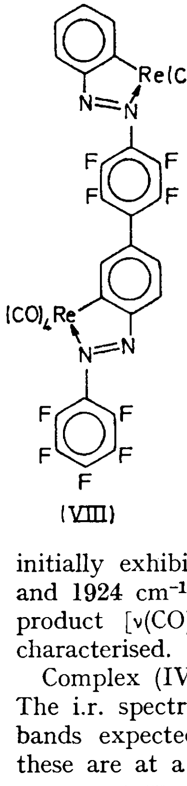
(V) X = H

(VI) X = F

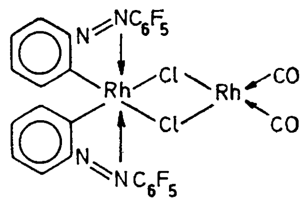


(IX) X = H

(X) X = F



(VIII)



(XII)

Complex (IV) was identified by the usual methods. The i.r. spectrum (Table 2) contained the four ν(CO) bands expected for a *cis*-$[LL^1M(CO)_4]$ complex, and these are at a higher frequency than those found for $[Mn(C_6H_4N{=}NPh)(CO)_4]$,[8] presumably as a result of removal of charge from the metal by the fluoroarylazo-group. The fingerprint region of the spectra of (IV) and of all the other *ortho*-metallated complexes contains a new band at *ca.* 770 cm^{-1}, attributed to an out-of-plane deformation of the *ortho*-disubstituted aromatic ring. The mass spectrum of (IV) was also consistent with the structure, and contained *inter alia* P^+ and $[P - n\mathrm{CO}]^+$ (n = 1—4) ions. The ^{1}H and ^{19}F n.m.r. spectra are discussed in detail below; the latter showed the 2 : 1 : 2 pattern of resonances characteristic of the C_6F_5 group.

In contrast, the reaction between pentafluoroazobenzene and $[Mn_2(CO)_{10}]$ afforded two complexes, albeit in low yields, one of which was (IV) above. The second complex (V), was distinguished by its mass spectrum, which exhibited a molecular ion at *m/e* 420, and the ^{19}F n.m.r. spectrum, which contained four signals of equal intensity, indicating the presence of four inequivalent fluorines in the ring. The signal at lowest field (112·6 p.p.m.) exhibited the large deshielding associated with the presence of a σ-bonded transition metal group *ortho* to the fluorine atom.[9]

The thermal reaction between 2*H*-nonafluoroazobenzene and $[Mn(CO)_5Me]$ afforded the fully-fluorinated chelate complex $[C_6F_5N{=}NC_6F_4Mn(CO)_4]$ (VI). This was identified in the usual ways, and characterised particularly by the mass spectrum (molecular ion at *m/e* 510, and ions formed by loss of CO groups) and the nine-line ^{19}F n.m.r. spectrum.

Using $[Re(CO)_5Me]$ and pentafluoroazobenzene, a slow reaction afforded a red complex, (VII), exactly analogous to (IV), as the major product. A second complex (VIII) was obtained from this reaction in small yield as a dark green-blue solid, soluble in nonpolar solvents. This complex was volatile (100°/0·1 mmHg), and the mass spectrum contained an apparent molecular ion at *m/e* 1120, which decomposed by loss of eight groups of 28 m.u. The isotope pattern corresponded to the presence of two rhenium atoms. The i.r. spectrum contained six ν(CO) bands. Unfortunately, the low yield of (VIII) precluded satisfactory n.m.r. spectra being obtained, and we were unable to characterise this complex fully. A possible structure for this complex is illustrated.

We were unable to isolate any new complexes from reactions between (I) and $[Re_2(CO)_{10}]$, $[Re(CO)_5]^-$, or $[Mn(CO)_5]^-$, even though the fluoroaromatic ring might have been expected to be susceptible to attack by the strongly nucleophilic rhenium anion.[4] Reaction with the latter may occur at the N=N double-bond (as found with organolithium compounds and azobenzene), but the intermediate so formed decomposed during work-up, regenerating (I) and $[Re_2(CO)_{10}]$.

(ii) *Ruthenium.* A red complex was isolated from the reaction between (I) and $[Ru_3(CO)_{12}]$. This formed red needles (IX), which gave a mass spectrum with a molecular ion at *m/e* 827, and stepwise loss of nine carbonyl groups. The isotope pattern was complex, but consistent with the presence of three ruthenium

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[8] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3204.

[9] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459.

TABLE 1

M.p. and analytical data

Compound	M.p. (t/°C)	Analyses (%) Found (calculated)			
		C	H	N	M [a]
(I) $C_6F_5N=NC_6H_5$	85—87	52·75 (53·0)	1·8 (1·85)	10·55 (10·3)	272 (272)
(II) $C_6F_5N=NC_6HF_4$	93—94	41·7 (41·85)	0·5 (0·3)	7·9 (8·15)	344 (344)
(III) p-$MeOC_6F_4N=NC_6H_5$	41—45	55·4 (54·9)	3·35 (1·75)	10·8 (9·85)	284 (284)
(IV) $[(C_6F_5N=NC_6H_4)Mn(CO)_4]$	77—79	43·95 (43·4)	0·9 (0·9)	6·4 (6·4)	438 (438)
(V) $[(C_6H_5N=NC_6F_4)Mn(CO)_4]$	145—148	46·2 (45·7)	1·3 (1·2)	6·8 (6·65)	420 (420)
(VI) $[(C_6F_5N=NC_6F_4)Mn(CO)_4]$	98—99	38·5 (38·6)	0·0 (0)	5·4 (5·5)	510 (510)
(VII) $[(C_6F_5N=NC_6H_4)Re(CO)_4]$	79—81	33·75 (33·7)	0·8 (0·7)	5·15 (4·95)	569 (569)
(IX) $[(C_6F_5N{\cdot}NHC_6H_4)Ru_3(CO)_9]$	150—152	30·65 (30·4)	0·7 (0·6)	3·4 (3·4)	827 (827)
(X) $[(C_6F_5N{\cdot}NHC_6F_4)Ru_3(CO)_9]$		28·4 (27·9)	0·1 (0·1)	3·5 (3·1)	902 (902)
(XI) $[(C_6F_5N=NC_6H_4)Pd(C_5H_5)]$	135—137	46·1 (46·2)	2·2 (2·0)	6·4 (6·3)	442 (442)
(XII) $[(C_6F_5N=NC_6H_4)_2RhCl_2Rh(CO)_2]$	210—212 d	35·8 (35·7)	1·15 (0·9)	6·4 (6·4)	819 [b] (875)

[a] Mass spectrometry. [b] $[P - 2CO]^+$.

TABLE 2

I.r. and n.m.r. data

Compound	$\nu(CO)/cm^{-1}$ [a]	Chemical shifts ^1H (τ)	^{19}F (p.p.m.)
(I) $C_6F_5N=NC_6H_5$		2·02—2·1m ($H^{2,6}$), 2·42—2·6 ($H^{3,4,5}$) [b]	149·9 ($F^{2,6}$), 152·8 (F^4), 162·0 ($F^{3,5}$) [c,d]
$C_6F_5N=NC_6F_5$			149·42 ($F^{2,6}$), 150·1 (F^4), 162·86 ($F^{3,5}$) [c]
(III) p-$MeOC_6F_4N=NC_6H_5$		2·19m ($H^{2,6}$), 2·56m ($H^{3,4,5}$), 5·89t (O*Me*; J_{HF}, 1·7 Hz) [e]	149·84 ($F^{2,6}$), 157·93 ($F^{3,5}$) [c]
$[(C_6H_5N=NC_6H_4)Mn(CO)_4]$	2075s, 1995vs, 1990sh, 1953vs, 1920w		
(IV) $[(C_6F_4N=NC_6H_4)Mn(CO)_4]$	2084s, 2009vs, 2000vs, 1961vs	1·50q (H^6), 1·77t (H^3), 2·50m ($H^{4,5}$) [b]	150·54 ($F^{2,6}$), 155·0 (F^4), 161·07 ($F^{3,5}$) [b,g]
(V) $[(C_6H_5N=NC_6F_4)Mn(CO)_4]$	2093m, 2017s, 2015sh, 1981s	2·35m (*Ph*) [b]	116·4 (F^2), 139·7 (F^5), 148·7 (F^3), 162·5 (F^4) [b]
(VI) $[(C_6F_5N=NC_6F_4)Mn(CO)_4]$	2101m, 2030vs, 2026sh, 1987s		
(VII) $[(C_6F_5N=NC_6H_4)Re(CO)_4]$	2096s, 2005s, 1994s, 1954s	1·54m (H^6), 1·84m (H^3), 2·55m ($H^{4,5}$) [b]	150·39 ($F^{2,6}$), 154·73 (F^4), 161·33 ($F^{3,5}$) [b,h]
(VIII) $[(C_{24}H_7F_9N_4)Re_2(CO)_8]$	2058w, 2026s, 2002w, 1976m, 1954w, 1938m		
(IX) $[(C_6F_5N{\cdot}NHC_6H_4)Ru_3(CO)_9]$	2071s, 2050s, 2018s, 1994w	2·93m (C_6*H_4*) [e]	
(X) $[(C_6F_5N{\cdot}NHC_6F_4)Ru_3(CO)_9]$	2085s, 2067vs, 2061s, 2030m, 2024s, 2021sh, 2008m		
(XI) $[(C_6F_5N=NC_6H_4)Pd(C_5H_5)]$		1·76dd (H^6), 2·14dd (H^3), 2·88td (H^5), 3·18td (H^4) [c]	148·4 ($F^{2,6}$), 155·0 (F^4), 160·9 ($F^{3,5}$) [c]
(XII) $[(C_6F_5N=NC_6H_4)_2RhCl_2Rh(CO)_2]$	2094vs, 2024s [i]		

[a] Cyclohexane. [b] $(CD_3)_2CO$. [c] CCl_4. [d] Coupling constants: $J_{2,3} = 16·5$; $J_{2,4} = 2·0$; $J_{2,5;\,3,6} = 8·0$; $J_{3,4} = 20·5$; $J_{2,6;\,3,5} =$ 3·0, 5·0 Hz. [e] CS_2. [f] Ref. 8. [g] Coupling constants: $J_{2,4} = 0$; $J_{3,4} = 21$ Hz. [h] Coupling constants: $J_{2,4} = 3·2$; $J_{3,4} = 21·0$ Hz. [i] $CHCl_3$.

atoms, and analysis confirmed the formulation of (IX) as $[Ru_3(CO)_9(C_6F_5N_2C_6H_5)]$. The i.r. spectrum contained four strong ν(CO) bands, and was generally similar to that of $[Ru_3(CO)_9(Ph_2N_2)]$,[10] which is thought to have an *o*-semidine-derived structure. The small amount of material obtained was enough only to give a ^1H n.m.r. spectrum containing a complex resonance between τ 2·7—3·1 unlike that of the usual *ortho*-metallated

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[10] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1971, **31**, 275.

complexes; the ^{19}F n.m.r. spectrum confirmed the presence of the C_6F_5 group. A similar reaction with 2*H*-nonafluoroazobenzene afforded the analogous product $[Ru_3(CO)_9(C_6F_5N{\cdot}NHC_6F_4)]$ (X). Both complexes were obtained in only low yields, possibly as a result of the less favourable migration of a C_6F_5N fragment compared to the C_6H_5N moiety.

Pentafluoroazobenzene reacted with palladium(II) chloride in methanol to give an insoluble orange precipitate, presumably $[\{Pd(C_6H_4N{:}NC_6F_5)Cl\}_2]$, although it was not characterised. Treatment of the solid with thallium(I) cyclopentadienide, however, afforded deep blue $[Pd(C_6H_4N{=}NC_6F_5)(C_5H_5)]$ (XI), which was fully characterised by analysis and spectroscopic methods. Thus the ^{1}H n.m.r. spectrum contained signals for the aromatic protons (see below), and a sharp singlet at τ 4·32 for the cyclopentadienyl protons. The ^{19}F n.m.r. spectrum contained the usual 2 : 1 : 2 pattern of resonances. In the mass spectrum peaks at *m/e* 442 and 377 corresponded to the molecular ion and $[P - C_5H_5]^+$, respectively.

A reaction between (I) and $[\{Rh(CO)_2Cl\}_2]$ afforded magenta crystals of $[\{RhCl(C_6H_4N{=}NC_6F_5)(CO)\}_2]$ (XII) containing two ν(CO) bands in its i.r. spectrum. The structure is presumably analogous to that found for the corresponding azobenzene derivative, in which a $Rh(C_6H_4N{=}NPh)_2$ group is linked to a $[Rh(CO)_2]$ moiety *via* two chlorine bridges.[11] The mass spectrum of (XII) does not contain a molecular ion; the ion at highest *m/e* corresponds to $[P - 2CO]^+$.

Nuclear Magnetic Resonance Spectra (*Table* 2).—The ^{1}H n.m.r. spectra of the parent azobenzenes contain aromatic resonances between τ 2·0 and 2·6 appearing as complex multiplets, and deserve no further comment. Those of the manganese and rhenium complexes (IV) and (VII) are similar, and consist of two low-field signals, at τ 1·5 and 1·8 (intensity 1H each), with a higher-field resonance at τ 2·5 (intensity 2H). Under high resolution, the signals are complex, and appear to be best described as an AMXX′ system. Decoupling experiments suggested that the lowest field signal is the proton adjacent to the azo-group; the second resonance is *ortho* to the metal; and the signal corresponding to two protons arises from the two '*meta*' protons of the ring.

Substitution of the sub-group VII elements by the $Pd(C_5H_5)$ group results in a shift of the signals in (XI) to higher field by some 0·5 p.p.m., and reflects the different electronic properties of this group. In addition, the two-proton signal at highest field is resolved into two separate resonances, and the whole spectrum is now that expected for the four-spin AMPX system. The lowest field signals are double doublets, while the two resonances at higher field are both triplets of doublets. Spin–spin decoupling experiments allow the four signals to be assigned to H^5, H^2, H^4, and H^3, respectively, in order of increasing field strength.

The ^{19}F n.m.r. spectra of the ligands show the three types of fluorine normally found in a C_6F_5 group. For (I), the *ortho* and *para* fluorine resonances lie close together, while the signal due to the *meta* fluorines is well upfield. In the methoxy-compound (III), the two-line pattern found for a *p*-C_6F_4XY group occurs at 150 and 158 p.p.m., the latter signal readily being assigned to the fluorines *ortho* to the OMe group by the small quartet coupling to the methoxy-protons.[12]

Complexes containing metallated non-fluorinated rings show all three resonances well separated, at *ca.* 150, 155, and 161 p.p.m. for F^{2,6}, F^4, and F^{3,5} respectively. The effect of the metal group is most marked on the chemical shift of F^4, which moves some 3—5 p.p.m. upfield. On the other hand, whereas the chemical shift of the proton reflects the different metals, they have no effect on the fluorine resonances. Evidently the metal–azo-group is too far removed for any significant shielding or deshielding effects of different metals to be detected.

Complex (V) shows four resonances in the ^{19}F n.m.r. spectrum, at 116·4, 139·7, 148·7, and 162·5 p.p.m. The lowest field resonance is in the region normally associated with fluorine nuclei *ortho* to transition-metal groups, and is thus assigned to F^2. This resonance is a quartet, which arises by coupling to the fluorine atoms at 140 p.p.m. and at 149 p.p.m. The magnitude of the coupling to the latter signal indicates that the fluorine is *ortho* to F^2, and hence this resonance can be assigned to F^3. The signal at highest field appears as a triplet, being coupled equally to F^3 and to F^5 (20 Hz), and can be assigned to F^4. The remaining two signals are complex; F^5 resonates at 140 p.p.m., and F^3 at 149 p.p.m.

Conclusions.—We have shown that metallation by displacement of fluorine is possible although where hydrogen can be eliminated this reaction takes precedence. The fluorine atom may be eliminated as HF, or as some manganese fluoride species. Other studies [13] indicate that elimination of molecular hydrogen may not, in fact, occur. For example, azobenzene cannot be metallated in a reaction with $[Ru(C_5H_5)(PPh_3)_2H]$, nor does that compound undergo an intramolecular metallation reaction after several hours at 140 °C, although both $[Ru(C_5H_5)(PPh_3)_2Me]$ and $[Ru(C_5H_5)(PPh_3)_2Cl]$ accomplish both reactions with ease. Consequently, we now envisage the metallation of azobenzene with decacarbonyl dimanganese as proceeding with the elimination of $[Mn(CO)_5H]$, which takes no further part in the reaction:

$$C_6H_5N{=}NC_6H_5 + [Mn_2(CO)_{10}] \longrightarrow [(C_6H_5N{=}NC_6H_4)Mn(CO)_4] + [Mn(CO)_5H] + CO$$

This may also provide an explanation for the consistently low yields of metallated product obtained in this reaction.[8]

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[11] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **40**, 393; R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 2141.

[12] J. Burdon, *Tetrahedron*, 1965, **21**, 1101.

[13] M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, unpublished results.

In the present case, where two products are obtained, a possible reaction course is the following

$$C_6F_5N{=}NC_6H_5 + [Mn_2(CO)_{10}] \longrightarrow$$

$$[(C_6F_5\overline{N{=}NC_6H_4)M}n(CO)_4] + [Mn(CO)_5H] + CO$$

$$C_6F_5N{=}NC_6H_5 + [Mn(CO)_5H] \longrightarrow$$

$$[(C_6H_5\overline{N{=}NC_6F_4)M}n(CO)_4] + HF + CO$$

with the elimination of the *ortho*-fluorine as hydrogen fluoride.

We have attempted to use the well known stability and high lattice energy of Me_3SnF [14] as a driving force for the fluorine-abstraction reaction, in a reaction between $[Mn(SnMe_3)(CO)_5]$ and decafluoroazobenzene. However, the expected product, $[(C_6F_5\overline{N{=}NC_6F_4)M}n(CO)_4]$, was not obtained, although it can be prepared from 2*H*-nonafluoroazobenzene (see above).

EXPERIMENTAL

Spectra were obtained with Perkin-Elmer 257 (i.r.), Varian Associates HA 100 (^1H and ^{19}F n.m.r.), and A.E.I. MS 902 (m.s.) instruments. Reactions were generally run under nitrogen, but no special precautions were taken to exclude oxygen during work-up. Chromatography was with columns of Florisil, initially packed in light petroleum (b.p. 40—60 °C).

Preparation of Azobenzenes.—(i) 2,3,4,5,6-*Pentafluoroazobenzene* (I). Pentafluoronitrosobenzene (1·0 g, 5·3 mmol) (Bristol Organics Ltd.) and aniline (1·0 ml, 11 mmol) were separately dissolved in glacial acetic acid (15 ml), and the ice-cold solutions were mixed. After being stirred for 2 h, the solution was allowed to warm to room temperature, neutralised with solid $NaHCO_3$, and then extracted with diethyl ether (4 × 50 ml). Chromatography of the concentrated extract gave a yellow-orange solid, eluted with light petroleum (b.p. 40—60°), purified by sublimation (50—60 °C/0·1 mmHg) to give orange *needles* of the product (I) (0·83—1·10 g, 60—80%).

(ii) 2H-*Nonafluoroazobenzene* (II). Pentafluoronitrosobenzene (500 mg, 2·6 mmol) and *o*-$HC_6F_4NH_2$ (400 mg, 2·5 mmol) in glacial acetic acid (10 ml) were refluxed for 30 min. The initial green colour changed to dark brown. Neutralisation with $NaHCO_3$, extraction with diethyl ether (4 × 50 ml), followed by chromatography and crystallisation from light petroleum, afforded orange crystals of 2H-*nonafluoroazobenzene* (II) (135 mg, 15%).

(iii) 2,3,5,6-*Tetrafluoro*-4-*methoxyazobenzene* (III). A mixture of (I) (300 mg, 1·1 mmol) and an excess of sodium methoxide (200 mg, 3·7 mmol) was refluxed in methanol (3 h). Chromatography of the product afforded an orange band (eluted with light petroleum), purified by sublimation to give an orange *solid* (III) (156 mg, 50%).

Reactions of 2,3,4,5,6-*Pentafluoroazobenzene.*—(i) *With* $[Mn(CO)_5Me]$. A mixture of $[Mn(CO)_5Me]$ (500 mg, 2·34 mmol) and pentafluoroazobenzene (647 mg, 2·38 mmol) was refluxed in heptane (b.p. 95—100 °C) (20 h). Chromatography and crystallisation of the deep red fraction (light petroleum–ether) afforded crystals of *tetracarbonyl*-(2,3,4,5,6-*pentafluorophenylazo*)*phenyl*-2′C,N-*manganese* (IV) (370 mg, 30%).

(ii) *With* $[Mn_2(CO)_{10}]$. A mixture of decacarbonyldimanganese (370 mg, 0·97 mmol) and pentafluoroazobenzene (500 mg, 1·84 mmol) was refluxed in heptane (50 ml) for 48 h. Chromatography afforded complex (IV) (65 mg, 8%), together with dark red crystals of *tetracarbonyl*(*phenylazo*)-2,3,4,5-*tetrafluorophenylmanganese* (V) (77 mg, 10%).

(iii) *With* $[Re(CO)_5Me]$. A mixture of $[Re(CO)_5Me]$ (240 mg, 0·7 mmol) and pentafluoroazobenzene (220 mg, 0·8 mmol) was refluxed in heptane (51 h). Chromatography of the product gave a small amount of unchanged ligand, followed by a deep orange band containing *complex* (VII) (150 mg, 37·5%), both eluted with diethyl ether, and a deep blue band, eluted with light petroleum–diethyl ether (98/2), which afforded the deep blue dichroic binuclear complex (VIII) (20 mg, 2·5%).

(iv) *With* $[Ru_3(CO)_{12}]$. Dodecacarbonyltriruthenium (500 mg, 0·95 mmol) and pentafluoroazobenzene (800 mg, 2·95 mmol) were refluxed in light petroleum (b.p. 95—100 °C) (50 ml) for 3 h. Work-up followed by chromatography afforded unchanged ligand and $[Ru_3(CO)_{12}]$, eluted with light petroleum; these were followed by a red fraction with 50 : 1 light petroleum–diethyl ether recrystallised to give red *needles* of (IX) (81 mg, 10%). Acetone gave a red-brown fraction, which afforded dark-coloured shiny crystals (150 mg), m.p. >350 °C, which were not further characterised.

(v) *With* $PdCl_2$. Pentafluoroazobenzene (560 mg, 2·05 mmol) was added to a suspension of $PdCl_2$ (350 mg, 2·0 mmol) in methanol (50 ml), and the mixture was stirred 3 h. The orange precipitate of $[\{\overline{Pd(C_6H_4N}{:}NC_6F_5)Cl\}]$ (720 mg, 90%) (characterised by i.r. spectroscopy only) was washed with diethyl ether. Part (500 mg) was added to a suspension of thallium cyclopentadienide (500 mg, 1·84 mmol) in tetrahydrofuran (50 ml) and the mixture refluxed (1 h). Filtration, evaporation, and chromatography afforded a dark blue band, crystallised from light petroleum to give dark blue *crystals* of $[\overline{Pd(C_6H_4N}{:}NC_6F_5)(C_5H_5)]$ (XI) (485 mg, 91%).

(vi) *With* $[\{RhCl(CO)_2\}_2]$. A mixture of $[\{RhCl(CO)_2\}_2]$ (300 mg, 0·79 mmol) and pentafluoroazobenzene (600 mg, 2·21 mmol) was refluxed in light petroleum (b.p. 95—100°) (50 mmol) for 9 h. Removal of solvent, extraction with CH_2Cl_2, and chromatography gave an orange band containing pentafluoroazobenzene (eluted with light petroleum) and a red fraction (with 1 : 1 light petroleum–ether) which afforded magenta *crystals* of $[\{\overline{RhCl(C_6H_4N{=}N}C_6F_5)(CO)\}_2]$ (XII) (260 mg, 37·5%).

Reactions of 2H-*Nonafluoroazobenzene.*—(i) *With* $[Mn(CO)_5Me]$. A mixture of $[Mn(CO)_5Me]$ (105 mg, 0·5 mmol) and nonafluoroazobenzene (172 mg, 0·5 mmol) in light petroleum (b.p. 95—100°) (50 ml) was refluxed for 4 h. Chromatography of the concentrated solution gave a red band (19 : 1 light petroleum–diethyl ether), which was crystallised to give magenta *crystals* of $[\overline{Mn(C_6F_4N{=}N}C_6F_5)(CO)_4]$ (VI) (35 mg, 14%).

(ii) *With* $[Ru_3(CO)_{12}]$. Refluxing a solution of $[Ru_3(CO)_{12}]$ (200 mg, 0·31 mmol) and nonafluoroazobenzene (75 mg, 0·22 mmol) in light petroleum (b.p. 95—100 °C) (25 ml) for 4 h, followed by chromatography and crystallisation (light petroleum), afforded red *crystals* of complex (X) (11 mg, 5·6%).

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