Cyclometallation Reactions. Part 16.[1] Some Reactions of η-Cyclopentadienylruthenium Phosphine Complexes

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ortho-Metallation reactions of several η-cyclopentadienylruthenium complexes are described. The complex $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ affords $[Ru(C_6H_4PPh_2)(\eta\text{-}C_5H_5)(PPh_3)]$, which with hexafluorobut-2-yne gives $[Ru\{[C(CF_3):C(CF_3)]_2C_6H_4PPh_2\}(\eta\text{-}C_5H_5)]$. The triphenyl phosphite complex $[Ru(\eta\text{-}C_5H_5)Cl\{P(OPh)_3\}_2]$ on heating yields $[Ru\{C_6H_4OP(OPh)_2\}(\eta\text{-}C_5H_5)\{P(OPh)_3\}]$. With azobenzenes, *m*-$RC_6H_4N:NPh$ (R = H, Me, OMe, CO_2Et, or CF_3), the complex $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ yields a mixture of isomers $[Ru(C_6H_3YN:NC_6H_4)Z\text{-}(\eta\text{-}C_5H_5)(PPh_3)]$ (Y = H, Z = R; or Y = R, Z = H). Using *m*-$RC_6H_4N:NC_6F_5$ (R = H, Me, or CF_3) the complexes $[Ru(C_6H_3RN:NC_6F_5)(\eta\text{-}C_5H_5)(PPh_3)]$, $[Ru(C_6F_4N:NC_6H_4R)(\eta\text{-}C_5H_5)(PPh_3)]$, and $[Ru(C_6F_4N:NC_6H_3R\cdot C_6H_4\text{-}PPh_2)(\eta\text{-}C_5H_5)]$ were formed, whilst from $C_6F_5N:NC_6F_5$ only $[Ru(C_6F_4N:NC_6F_5)(\eta\text{-}C_5H_4C_6H_4PPh_2)]$ was isolated Speculation on the mechanism of the fluorine-elimination reaction is given some credence by the synthesis of $[Ru(\eta\text{-}C_5H_5)F(PPh_3)_2]$.

WE have briefly mentioned elsewhere [2] that a common by-product from reactions of $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ is the *ortho*-metallated complex $[Ru(C_6H_4PPh_2)(\eta\text{-}C_5H_5)(PPh_3)]$, (I), formed by loss of methane in an intramolecular process which often favourably competes with other reactions. This process is similar to metallation of a PPh_3 ligand observed in the chemistry of the rhodium

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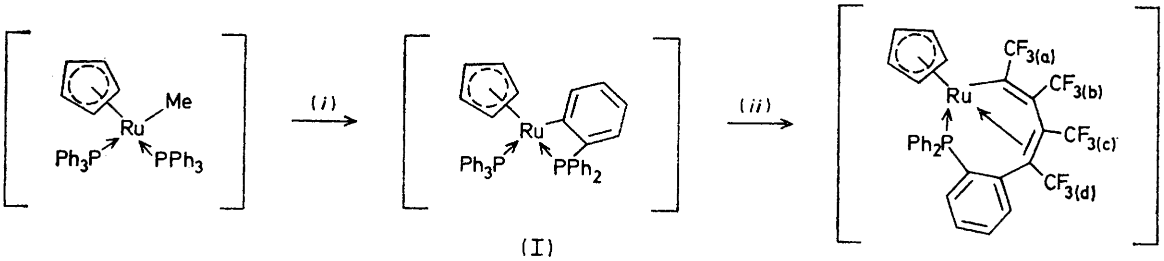
[1] Part 15, R. L. Bennett, M. I. Bruce, and I. Matsuda, *Austral. J. Chem.*, 1975, **28**, 2307.

[2] M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **40**, C39.

complex $[RhMe(PPh_3)_3]$.[3] Here we describe the formation of (I) in more detail, together with other metallation reactions involving complexes containing the $[Ru(\eta\text{-}C_5H_5)]$ group.

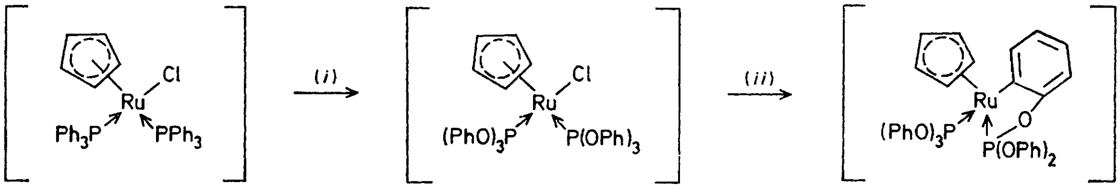
RESULTS



(I)

(II)

SCHEME 1 (*i*), Refluxing decalin, $-CH_4$; (*ii*), $C_2(CF_3)_2$



(IV)

(III)

SCHEME 2 (*i*), $P(OPh)_3$; (*ii*), refluxing decalin, $-HCl$

Phosphorus-donor Ligands.—When either the methyl complex $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$, or the corresponding pale yellow benzyl derivative $[Ru(CH_2Ph)(\eta\text{-}C_5H_5)(PPh_3)_2]$, was briefly heated under reflux in decalin, complex (I) was formed in high yield (Scheme 1). The ^1H n.m.r. spectrum showed resonances at τ 3.04(m) for the aromatic protons and at τ 5.65(s) (C_5H_5); the former signal was broadened to higher field, a typical feature of complexes containing an *ortho*-metallated phenyl group. The mass spectrum contained a parent ion, centred at *m/e* 690.

Complex (I) reacted with $C_2(CF_3)_2$ to yield a bis insertion product, characterised as $[Ru\{[C(CF_3){:}C(CF_3)]_2C_6H_4PPh_2\}(\eta\text{-}C_5H_5)]$, (II). In the i.r. spectrum a medium-intensity band at 1 647 cm^{-1} is assigned to $\nu(C{=}C)$, and strong absorptions between 1 250 and 1 100 cm^{-1} are typical of $\nu(CF)$ vibrations. The ^{19}F n.m.r. spectrum contained four resonances of equal intensity, and the chemical shifts [relative to CCl_3F at 50.6(q) $(CF_{3(d)})$ $J(F_dF_c)$ 12.0; 54.9(m), $(CF_{3(c)})$, $J(F_cF_d)$ 12.0, $J(F_aF_b)$ 9.0 of equal intensity; 55.6(q) $(CF_{3(a)})$, $J(F_aF_b)$ 9.0; and 61.65 (spt) p.p.m. $(CF_{3(b)})$, $J(F_bF_a)$ 9.0, J (F_bF_c) 9.0 Hz] and coupling constants are consistent with the presence of two *cis*-$C(CF_3){:}C(CF_3)$ groups. We suggest that this complex contains the 4-[2′-(diphenylphosphino)phenyl]-butadienyl ligand shown in (II), chelating *via* Ru–C σ, C_2–Ru η^2, and P–Ru σ-donor bonds. Thus the formation of (II) parallels the reaction between C_2Ph_2 and $[Rh(C_6H_4PPh_2)(PPh_3)_2]$ to give $[Rh(CPh:CPhCPh:CPhC_6H_4PPh_2)(PPh_3)]$, the structure of which was established by single-crystal *X*-ray diffraction.[4]

After the chloro-complex $[Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2]$ was briefly heated with triphenyl phosphite in refluxing decalin, chromatography resulted in two complexes (Scheme 2). The first complex was characterised as the *ortho*-metallated derivative $[Ru\{C_6H_4OP(OPh)_2\}(\eta\text{-}C_5H_5)\{P(OPh)_3\}]$, (III). The i.r. spectrum contained bands characteristic of a metallated phosphite. In the ^1H n.m.r. spectrum the aromatic proton signal was broadened considerably to higher field. In the mass spectrum, a parent ion centred at *m/e* 786 fragmented by loss of OPh groups. Complex (IV) was readily identified as the ligand-exchanged derivative $[Ru(\eta\text{-}C_5H_5)Cl\{P(OPh)_3\}_2]$. Complex (III) was also obtained by heating (IV) under reflux in decalin with dicyclohexylethylamine. The amine hydrochloride rapidly precipitated and (III) was obtained in high yield. Complex (III) contains a five-membered chelate ring (RuCCOP), and in consequence it is not expected to be very reactive. In contrast to (I), which contains the four-membered RuCCP ring, no reaction between (III) and $C_2(CF_3)_2$ was observed after heating the reactants at 100 °C for 1 week.

Nitrogen-donor Ligands.—In previous work,[5] we described the preparation of chelating 2-(phenylazo)phenyl complexes $[Ru(C_6H_4N{:}NPh)(\eta\text{-}C_5H_5)L]$ ($L = CO$ or PPh_3), isolated from reactions between $[RuMe(CO)_2(\eta\text{-}C_5H_5)]$ and azobenzene, or between $[\{Ru(C_6H_4N{:}NPh)(CO)_2Cl\}_2]$ and $Na(C_5H_5)$, followed by treatment of the products with PPh_3. A reaction between $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ and azobenzene, at 100 °C in light petroleum, proved to be a third route to $[Ru(C_6H_4N{:}NPh)(\eta\text{-}C_5H_5)(PPh_3)]$, (V; $R = H$), accompanied by formation of a small amount of complex (I).

We have demonstrated that reactions of *meta*-substituted

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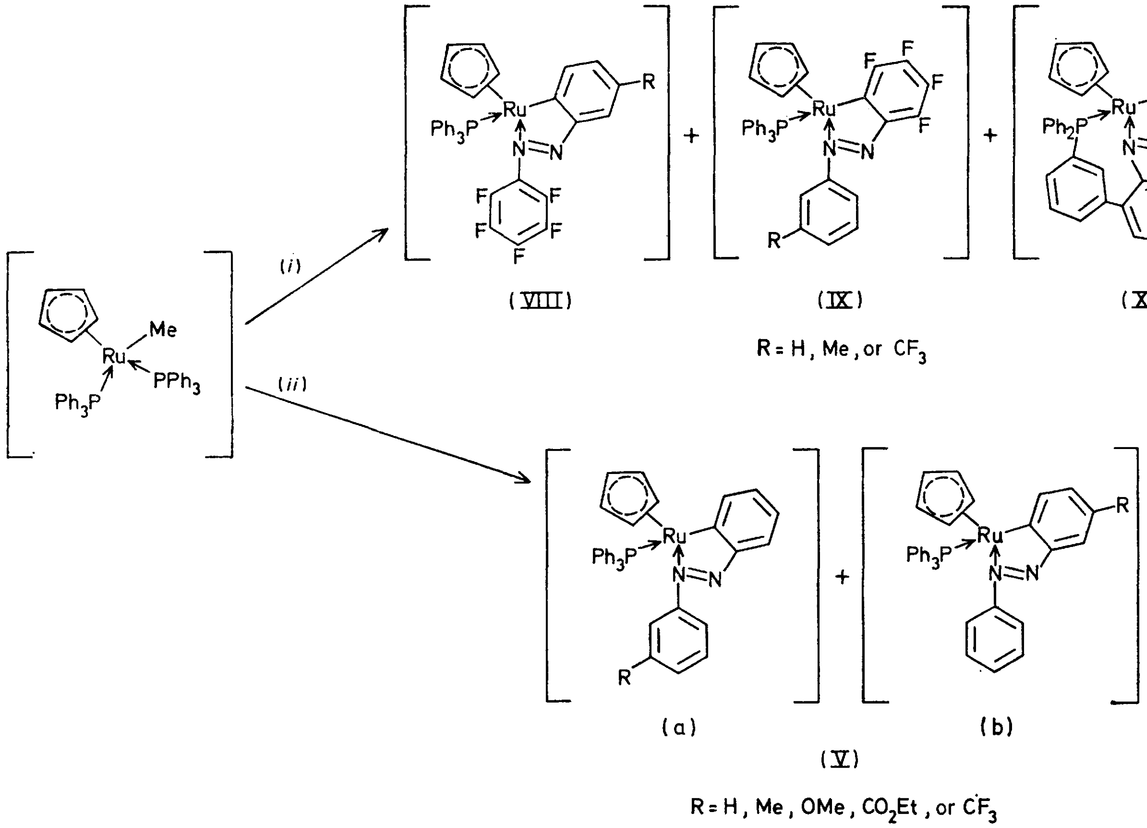
[3] W. Keim, *J. Organometallic Chem.*, 1968, **14**, 179.

[4] J. S. Ricci and J. A. Ibers, *J. Organometallic Chem.*, 1971, **27**, 261.

[5] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, (*a*) *J. Chem. Soc.* (*A*), 1970, 3204; (*b*) *ibid.*, 1971, 2820.

azobenzenes may provide useful information on the nature and course of metallation reactions.[6] Accordingly we have also studied the reactions of $[\mathrm{RuMe}(\eta\text{-}C_5H_5)(PPh_3)_2]$ with a series of these azo-compounds (Scheme 3). However, in contrast to previous work, from which single products, or a simple mixture of isomers, were obtained, these reactions were complex. Moreover, with one exception, the total product yield did not exceed 13%, so that we were unable to deduce any mechanistic information from these results. The new species (V) obtained from $m\text{-}RC_6H_4N{:}NPh$ (R = Me, OMe, CO_2Et or CF_3), were all characterised as isomeric mixtures of the type $[\mathrm{Ru}(C_6H_4N{:}NC_6H_4R\text{-}m)(\eta\text{-}C_5H_5)(PPh_3)]$, (Va), and $[\mathrm{Ru}(C_6H_3R\text{-}m\text{-}N{:}NPh)(\eta\text{-}C_5H_5)(PPh_3)]$, (Vb), by analysis and ^1H n.m.r. spectra. The spectra, however, did not unequivocally give the proportions of each isomer formed. Thus, the ^1H n.m.r. spectrum of the product mixture (V; R = Me) revealed that two isomers were present in a *ca.* 1 : 2 ratio. Reference to the ^1H n.m.r. spectrum of (V; R = H) further suggests that isomer (Vb) is metallated in the substituted ring. The three sets of resonances found for the products (V; R = OMe and CF_3) indicated that all three possible isomers are formed in these two reactions.



SCHEME 3 (*i*), $m\text{-}RC_6H_4N{:}NC_6F_5$; (*ii*), $m\text{-}RC_6H_4N{:}NPh$

The reaction between $3,5\text{-}(MeCO_2)_2C_6H_3N{:}NPh$ and $[\mathrm{RuMe}(\eta\text{-}C_5H_5)(PPh_3)_2]$ afforded two isomeric complexes, which it was possible to separate chromatographically, in addition to the usual small amount of (I). The first isomer was characterised as $[\mathrm{Ru}\{C_6H_4N{:}NC_6H_3(CO_2Me)_2\}(\eta\text{-}C_5H_5)(PPh_3)]$, (VIa), in which the Ph group has been metallated. In the ^1H n.m.r. spectrum a single resonance at τ 6.02 indicated that both CO_2Me groups are equivalent, as required for structure (VIa). The second isomer (VIb) is the analogous complex in which the polysubstituted ring has been metallated. The i.r. spectrum exhibited bands at 1 714 [ν(CO)] and 1 587 cm^{-1}; bands characteristic of the metallated ring were not found, presumably because the two extra substituents affect the usual pattern. The two resonances found at τ 6.15 and 6.25 confirm the inequality of the two CO_2Me groups in (VIb). This isomer was formed in only low yield after 20 h reflux, and shorter reaction times gave (VIa) as the only product isolated. Steric hindrance by the CO_2Me groups may explain this result. We were unable to form a complex such as (VII) on prolonged heating.

We investigated the reactions between the fluorinated azobenzenes $m\text{-}RC_6H_4N{:}NC_6F_5$ (R = H, OMe, CO_2Me, or CF_3) and the methylruthenium complex, from two points of view. The first was a consideration that the presence of the C_6F_5 group might simplify the ^1H n.m.r. spectra of any products metallated in the substituted phenyl ring, and allow an exact assignment of structure. In addition, our earlier finding [6] that a nucleophilic reaction path may be followed in *ortho*-metallation reactions involving electron-rich metal substrates encouraged us to seek reactions of this type in which aromatic fluorines were displaced, one example of which has been described by us previously.[7] We were

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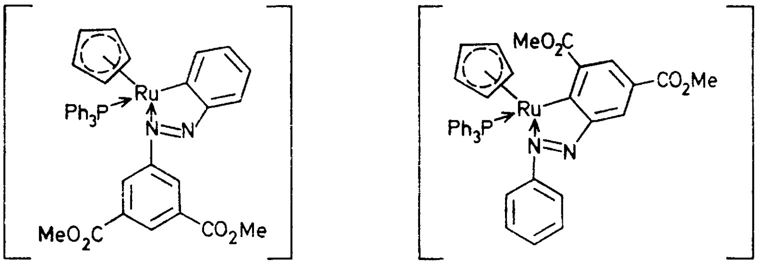
[6] M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 558.

[7] M. I. Bruce, B. L. Goodall, G. Sheppard, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 591.

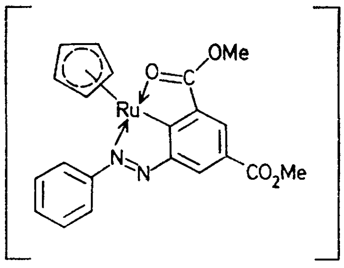
successful on both counts, and in addition a third pattern of reactivity was found, namely linking of cyclopentadienyl and phenyl groups. Some of these results have been briefly mentioned.[8]

The dark green solution obtained on heating a mixture of $[\mathrm{RuMe(\eta\text{-}C_5H_5)(PPh_3)_2}]$ and $\mathrm{PhN{:}NC_6F_5}$ in refluxing light petroleum afforded three products which were separated chromatographically. First to be eluted was pale green $[\overline{\mathrm{Ru(C_6H_4N{:}N}}\mathrm{C_6F_5)(\eta\text{-}C_5H_5)(PPh_3)}]$ (VIII; R = H), entirely analogous to complex (V) above, and formed by metallation of the Ph ring. The ^{19}F n.m.r. spectrum exhibited the three signals characteristic of a $\mathrm{C_6F_5}$ group, while the ^{1}H n.m.r. contained resonances in the aromatic region, partially overlapped by the $\mathrm{PPh_3}$ signals, typical of *ortho*-metallated complexes. The second product was also readily characterised, as the metallated complex $[\overline{\mathrm{Ru(C_6F_4N{:}N}}\mathrm{Ph)(\eta\text{-}C_5H_5)(PPh_3)}]$, (IX; R = H), formed by fluorine abstraction. The ^{19}F n.m.r. spectrum contained four signals at *ca.* 118, 156, 159, and 168 p.p.m. (upfield from $\mathrm{CCl_3F}$), with fine structure expected for an AMPX system. The marked deshielding of the fluorine *ortho* to the σ-bonded ruthenium [9] confirmed that the $\mathrm{C_6F_5}$ ring had been metallated. The molecular ion was centred at *m/e* 682. The third complex contained a parent ion in its mass spectrum only two units lower than that found for (IX; R = H). The total signal intensity in the ^{1}H n.m.r. spectrum corresponded to 18 aromatic protons (measured with reference to the sharp spike for the $\mathrm{C_5H_5}$ protons at τ 5.12). The ^{19}F n.m.r. spectrum contained four signals at 118, 143, 158, and 168 p.p.m., three of which are similar to those found in the spectrum of (IX; R = H), while the fourth assigned to $\mathrm{F_b}$ was *ca.* 13 p.p.m. downfield. We propose structure (X; R = H) for this complex. This satisfies all the spectroscopic data, the downfield shift observed for $\mathrm{F_b}$ being a result of modification of the electronic properties of the azo-group by the co-ordinated phosphine ligand. The structure is also supported by the observation of an ion cluster centred at *m/e* 420, and corresponding to loss of a $\mathrm{PC_6H_3Ph_2}$ group from the parent; normally, loss of the intact $\mathrm{PPh_3}$ group is found in this type of complex.



(a) (b)

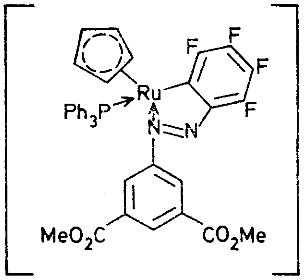
(VI)



(VII)

Extension of the reactions of $[\mathrm{RuMe(\eta\text{-}C_5H_5)(PPh_3)_2}]$ to $\mathrm{C_6F_5N{:}NC_6H_4R}$-*m* (R = Me and $\mathrm{CF_3}$) afforded in each case three complexes which were characterised as analogues of (VIII)—(X). In both cases, the phenyl-linked derivatives (X; R = Me and $\mathrm{CF_3}$) were formed in lower yields than the simple fluorine-substituted complexes (IX). *ortho*-Metallation of the substituted phenyl group in (VIII; R = Me and $\mathrm{CF_3}$) can form two possible isomers, depending on whether the substituent R becomes *ortho* or *para* to the metal. Isomers are also possible with (X; R = Me and $\mathrm{CF_3}$). The n.m.r. results, however, showed that only one isomer is formed in every case. In the structural formulae (VIII; R = Me and $\mathrm{CF_3}$) we have arbitrarily chosen the isomer with the substituent *para* to the metal. Indeed with the electron-donating methyl substituent, the most likely position for metallation by an electron-rich species is *para* to the methyl group, to give (VIII; R = Me). There was no significant difference in the Me chemical shifts of (VIII) and (IX; R = Me) (τ 7.66 and 7.77, respectively), suggesting that there is little difference in their environments and, more specifically, that in (VIII; R = Me) the Me group is not *ortho* to the metal atom. Similarly two isomers are possible for (VIII; R = $\mathrm{CF_3}$), but in this case also it is not possible to make an unequivocal assignment of the geometry of the one isomer shown to be present by n.m.r. methods. Possible steric effects suggest that metallation might occur in the second most favoured position, *i.e*, *para* to the $\mathrm{CF_3}$ group. The chemical shifts of the $\mathrm{CF_3}$ groups in the proton-substituted derivatives (VIII) and (IX) (R = $\mathrm{CF_3}$) were 62.3 and 62.8 p.p.m., confirming this hypothesis.

Only one complex was isolated from reaction between $[\mathrm{RuMe(\eta\text{-}C_5H_5)(PPh_3)_2}]$ and $3,5\text{-}\mathrm{(MeCO_2)_2C_6H_3N{:}NC_6F_5}$, the tetrafluoro-derivative $[\overline{\mathrm{Ru\{C_6F_4N{:}N}}\mathrm{C_6H_3(CO_2Me)_2\}(\eta\text{-}C_5H_5)(PPh_3)}]$, (XI). In the ^{1}H n.m.r. spectrum a sharp signal at τ 6.01 indicated both $\mathrm{CO_2Me}$ groups were equivalent; the ^{19}F n.m.r. spectrum contained four resonances, with similar parameters to those found for (IX; R = H). The absence of any complex metallated in the polysubstituted ring prob-



(XI)

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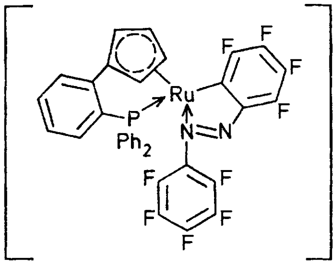
[8] M. I. Bruce, R. C. F. Gardner, B. L. Goodall, F. G. A. Stone, R. J. Doedens, and J. A. Moreland, *J.C.S. Chem. Comm.*, 1974, 185.

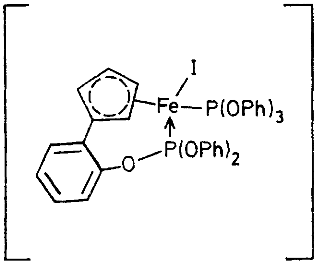
[9] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1457; F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *ibid.*, 1966, 1326.

ably results from the severe steric hindrance of the CO_2Me groups; the relative difficulty of attack on this ring has been noted above.

Finally, the reaction between $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ and decafluoroazobenzene, $C_6F_5N{:}NC_6F_5$, affords a single dark green crystalline complex, shown to have the unusual structure (XII) by a single-crystal *X*-ray diffraction study.[8] Bands in the i.r. spectrum at 1 640, 1 595, and 1 564 cm^{-1} can be assigned to the aromatic ring vibrations, and the strong band at 1 509 cm^{-1} is characteristic of a C_6F_5 group. A further absorption at 1 093 cm^{-1} indicates the *ortho*-disubstituted phenyl ring. In the ^1H n.m.r. spectrum the aromatic resonances were broadened to higher field, while the usual spike for the C_5H_5 group was replaced by four resonances each of intensity one. This indicates that the cyclopentadienyl group is substituted, and further that it is held in a rigid conformation by chelation of the complex ligand so formed. In the ^{19}F n.m.r. spectrum seven resonances were found. Three, at 148, 159, and 162 p.p.m., had the characteristic intensities and fine structure associated with C_6F_5 groups and are so assigned. The other four signals, at 116, 143, 157, and 167 p.p.m., arise from an AMPX system, and are generally similar to the other *ortho*-metallated C_6F_4 groups already discussed. In addition to a parent-ion cluster centred at *m/e* 770, the mass spectrum contained other ions corresponding to $[P - F]^+$ and $[P - PC_6H_4Ph_2]^+$. Complex (XII) is the first example of a complex obtained from the fully fluorinated azobenzene nucleus, although we have described $[\{\overline{Pd(C_6F_4N{:}N}C_6F_5)Cl\}_2]$ formed from $Li_2[PdCl_4]$ and $o\text{-}HC_6F_4N{:}NC_6F_5$.[7] It is also the first occasion on which the η-(2-diphenylphosphinophenyl)cyclopentadienyl ligand has been characterised, although the related complex (XIII) derived from triphenyl phosphite has long been known.[10]



(XII)



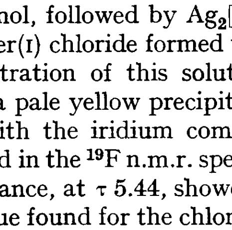
(XIII)

DISCUSSION

Several types of *ortho*-metallated complexes containing the $[Ru(\eta\text{-}C_5H_5)(PPh_3)]$ group have been prepared, and their formation is facilitated by the presence of the the σ-alkyl group. In particular, many reactions involving heating of $[RuR(\eta\text{-}C_5H_5)(PPh_3)_2]$ (R = Me or CH_2Ph) with a variety of reagents have been found to give (I), as well as the other complexes. We have also shown that dehydrochlorination of the analogous chloride is an efficient route to (III). The observed difference in reactivity found in reactions between (I) and (III) and $C_2(CF_3)_2$ can be correlated with the presence of four- and five-membered chelate rings, respectively.

In reactions with azobenzenes, complexes containing chelating (2-phenylazo)phenyl-*CN'* groups are readily obtained. However, the ready formation of tetrafluoro-derivatives in reactions with pentafluorophenylazo-compounds confirms the anticipated tendency for the low-valent electron-rich ruthenium group to enter into a nucleophilic *ortho*-metallation reaction with the fluorinated ring. We have speculated that the metallation of fluorinated azobenzenes which proceeds by fluorine abstraction, *e.g.* with $[Mn_2(CO)_{10}]$, may occur *via* formation of an unstable manganese carbonyl fluoride, or by formation of hydrogen fluoride.[7] In the present case, elimination of a ruthenium fluoride or perhaps MeF is possible and we sought to clarify the matter by an independent synthesis of the postulated fluoride complex $[Ru(\eta\text{-}C_5H_5)F(PPh_3)_2]$ (XIV).

The preparation of $[Ir(CO)F(PPh_3)_2]$ from the analogous chloride and $[NH_4]F$, followed by treatment with silver(I) carbonate, has been described.[11] When orange $[Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2]$ was added to a hot saturated solution of $[NH_4]F$ in methanol, followed by $Ag_2[CO_3]$, a flocculent precipitate of silver(I) chloride formed with a pale yellow supernatant. Filtration of this solution into aqueous $[NH_4]F$ afforded a pale yellow precipitate, characterised as (XIV). As with the iridium complex, the fluorine cannot be detected in the ^{19}F n.m.r. spectrum; the cyclopentadienyl resonance, at τ 5.44, showed the anticipated shift from the value found for the chloride (τ 5.99). The stability of (XIV) is not high, however. Attempted recrystallisations from methanol resulted in considerable



(XIV)

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[10] V. G. Andrianov, Y. A. Chapovskii, V. A. Semion, and Y. T. Struchkov, *Chem. Comm.*, 1968, 282.

[11] L. Vaska and J. Peone, *Chem. Comm.*, 1971, 418; G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *ibid.*, p. 758.

decomposition, and it was not recovered after chromatography on Florisil. Thus we are unable to determine whether this complex is formed during metallation reactions of fluorinated azobenzenes by cyclopentadienylruthenium complexes, since it would have been decomposed either during the reaction or on work-up.

Nevertheless, the formation of (XIV) as an isolable entity, under some conditions at least, provides plausible reaction paths for the formation of all three types of complex described above. Thus for $PhN{:}NC_6F_5$, for example, we have equations (1)—(3). In the case of decafluoroazobenzene, the unusual linking of the PPh_3 and C_5H_5 groups by elimination of two hydrogen atoms to give (XII) has a precedent in iron chemistry in the second ' isomer ' of the complex $[Fe(\eta\text{-}C_5H_5)I\{P(OPh)_3\}_2]$, shown by a single-crystal *X*-ray diffraction study[10] to have structure (XIII). We have also described the facile reaction of the cyclopentadienyl ring in a related reaction of the ruthenium complex $[Ru\{C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)(PPh_3)]$ with hexafluoroacetone.[12] In that case, we suggested that the reaction occurred as a result of the tertiary phosphine ligands back-bonding to the metal, increasing the electron density on the C_5 ring and thus rendering the ring more susceptible to attack by electrophilic reagents. In the present case, a similar explanation may be advanced; the different routes followed by azobenzene, pentafluoroazobenzene, and decafluoroazobenzene reflect the differences both in electronic properties and in steric requirements of the azo-ligands.

$$PhN{:}NC_6F_5 + [RuMe(\eta\text{-}C_5H_5)(PPh_3)_2] \xrightarrow[-PPh_3]{-CH_4} [\overline{Ru(C_6H_4N{:}N}C_6F_5)(\eta\text{-}C_5H_5)(PPh_3)] \quad (VIII;\ R = H) \quad (1)$$

$$\xrightarrow[-PPh_3]{-MeF} [\overline{Ru(C_6F_4N{:}N}Ph)(\eta\text{-}C_5H_5)(PPh_3)] \quad (IX;\ R = H) \quad (2)$$

$$PhN{:}NC_6F_5 + 2[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2] \xrightarrow[-PPh_3]{-CH_4} [\overline{Ru(C_6F_4N{:}NC_6H_4C_6H_4PPh_2})(\eta\text{-}C_5H_5)] \quad (X;\ R = H)$$
$$+ [Ru(\eta\text{-}C_5H_5)F(PPh_3)_2] \quad (XIV) \quad (3)$$

Thus with azobenzene the simple *ortho*-metallated complex (V; R = H) is formed, and is accompanied by some of the *ortho*-metallated phosphine (I), formed in a competitive reaction. With pentafluoroazobenzene, metallation of the Ph ring can occur by elimination of methane, while nucleophilic attack on the C_6F_5 ring by the electron-rich $[Ru(\eta\text{-}C_5H_5)(PPh_3)]$ group results in elimination of the *ortho*-fluorine atom by a route not yet determined. Also formed is the unusual complex (X; R = H) in which the PPh_3 ligand is linked to the Ph ring of the azo-ligand. Decafluoroazobenzene affords a complex, (XII), in which the C_6F_5 ring is metallated, as well as the link between the C_5 and C_6 rings mentioned above. A notable feature of the structure is the non-planar azo-ligand, probably as a result of interaction with the other ligands around the ruthenium atom.

EXPERIMENTAL

Spectra were recorded on Perkin-Elmer 257 or 457 (i.r.), Varian Associates HA100 (^1H n.m.r. at 100 MHz, ^{19}F n.m.r. at 94.1 MHz), or A.E.I.–G.E.C. MS902 spectrometers (mass; 70 eV ionising energy,* 8 kV accelerating potential, 150 μA trap current, and source temperature *ca.* 150 °C). Solvents were dried and distilled before use, and all reactions were carried out under a nitrogen atmosphere. Chromatography was on columns of Florisil (unless otherwise stated), initially packed in light petroleum.

Analyses are collected in Table 1, i.r. data in Table 2, and n.m.r. chemical shifts and coupling constants in Tables 3 and 4. Fluorine-19 chemical shifts are relative to CCl_3F (0.00 p.p.m.). The compounds $[RuR(\eta\text{-}C_5H_5)(PPh_3)_2]$ (R = Me,[13] CH_2Ph[14]), $m\text{-}XC_6H_4N{:}NC_6F_5$ (X = H, Me, OMe, CO_2Me, or CF_3),[7] and $C_6F_5N{:}NC_6F_5$[15] were prepared by literature methods; $3,5\text{-}(MeCO_2)_2C_6H_3N{:}NR'$ (R′ = Ph or C_6F_5) were obtained from reactions between R′NO and $3,5\text{-}(MeCO_2)_2C_6H_3NH_2$ [$(MeCO_2)_2C_6H_3N{:}NPh$, m.p. 142—143 °C, Found: C, 64.05; H, 4.6; N, 9.4%; *M* (mass spectrometry) 298. $C_{16}H_{14}N_2O_4$ requires C, 64.3; H, 4.7; N, 9.4%; *M* 298. $(MeCO_2)_2C_6H_3N{:}NC_6F_5$, m.p. 150 °C, Found: C, 49.4; H, 2.6; N, 6.9%; *M* (mass spectrometry) 388. $C_{16}H_9F_5N_2O_4$ requires C, 49.5; H, 2.3; N, 7.2%; *M* 388].

ortho-*Metallation Reactions involving Phosphorus-donor Ligands.*—(a) *Internal metallation in* $[RuR(\eta\text{-}C_5H_5)(PPh_3)_2]$ (R = Me *or* CH_2Ph). Chromatography (alumina) of the hot solution obtained on heating $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ (290 mg, 0.41 mmol) under reflux in decalin (10 cm³) for 5 min gave a yellow band, eluted with benzene, which yielded pale yellow *crystals of* $[\overline{Ru(C_6H_4PPh_2})(\eta\text{-}C_5H_5)(PPh_3)]$, (I) (235 mg, 84%). Alternatively, heating the benzyl complex (500 mg, 0.76 mmol) under reflux in decalin (10 cm³) for 20 min followed by chromatography afforded a pale yellow fraction [with light petroleum–diethyl ether (1 : 1)], from which complex (I) (88 mg, 20%) was obtained.

(b) *Preparation of triphenyl phosphite complexes.* A mixture of $[Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2]$ (500 mg, 0.77 mmol) and $P(OPh)_3$ (435 mg, 1.40 mmol) was heated under reflux in decalin (10 cm³) for 15 min. Chromatography afforded two fractions. Elution with benzene, evaporation, and crystallisation gave pale yellow *crystals* of $[\overline{Ru\{C_6H_4OP}(OPh)_2\}(\eta\text{-}C_5H_5)\{P(OPh)_3\}]$, (III) (81 mg, 15%). Elution with diethyl-ether–benzene gave orange *crystals* of $[RuCl(\eta\text{-}C_5H_5)\{P(OPh)_3\}_2]$, (IV) (135 mg, 24%).

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* 1 eV ≈ 1.60×10^{-19} J.

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TABLE 1

Analytical and m.p. data

Complex	M.p. (θ_c/°C)	Analysis [a](%) C	H	N	Other	M [a,b]
(I)	223—225	71.4	4.7	(P) 9.2	(Ru) 15.1	706 [c]
		(71.4)	(5.0)	(9.0)	(14.65)	(690)
(II)	245—250	49.4	2.7	(P) 4.0	(F) 29.0	752
		(48.7)	(2.5)	(4.0)	(29.7)	(752)
(III)	116—118	6.31	4.5	(P) 7.9		786
		(62.7)	(4.4)	(7.9)		(786)
(IV)	152—154	60.0	4.6	(P) 7.2	(Cl) 4.4	822
		(59.9)	(4.3)	(7.6)	(4.3)	(822)
(V; R = Me) [d]	145—148	68.85	4.9	4.6		624
		(69.4)	(5.0)	(4.95)		(624)
(V; R = OMe) [d]	144—148	67.95	5.3			640
		(67.6)	(4.9)			(640)
(V; R = CO_2Et) [d]	160—165	66.75	4.85	3.9		682
	(decomp.)	(66.95)	(4.9)	(4.1)		(682)
(V; R = CF_3) [d]	190—195	63.5	4.25	3.45		678
	(decomp.)	(63.8)	(4.2)	(4.15)		(678)
(VIa)	231—233	64.85	4.55	3.8		726
		(64.5)	(4.55)	(3.85)		(726)
(VIb)	201—205	64.05	4.6	3.9		726
	(decomp.)	(64.5)	(4.55)	(3.85)		(726)
(VIII; R = H)	183—185	60.5	3.6	4.0		700
		(60.0)	(3.45)	(4.0)		(700)
(IX; R = H)	245—247	61.5	3.7	3.9		682
		(61.7)	(3.7)	(4.1)		(682)
(X; R = H)	200—202	61.4	3.5	4.05		680
		(61.8)	(3.4)	(4.1)		(680)
(VIII; R = Me)	200—205	60.3	3.8	3.9		714
		(60.6)	(3.7)	(3.95)		(714)
(IX; R = Me)	225—227	62.15	3.85	3.9		696
		(62.15)	(3.9)	(4.0)		(696)
(X; R = Me)	152—156	63.2	3.75	4.1		694
		(62.2)	(3.65)	(4.05)		(694)
(VIII; R = CF_3)	195—197	57.2	3.25	3.45		768
		(56.4)	(3.05)	(3.65)		(768)
(IX; R = CF_3)	187—191	60.0	3.6	3.55	(F) 9.55	750
		(58.7)	(3.65)	(3.5)	(9.55)	(750)
(X; R = CF_3)	203—207	57.0	3.1	3.5		748
		(57.9)	(2.95)	(3.75)		(748)
(XI)	191—193	57.5	3.2	4.1		798
	(decomp.)	(57.7)	(3.25)	(3.75)		(798)
(XII)	225—230	55.4	2.35	3.7	(F) 21.0	770
	(decomp.)	(54.65)	(2.35)	(3.65)	(22.2)	(770)
(XIV)	115—120	69.35	4.95		(P) 8.74	
		(69.1)	(5.15)		(8.0)	

[a] Calculated values are given in parentheses. [b] From mass spectrometry. [c] From osmometry in C_6H_6. [d] Isomeric mixture (see text).

(c) *Reaction between* (I) *and* $C_2(CF_3)_2$. Complex (I) (350 mg, 0.51 mmol), hexafluorobut-2-yne (3 mmol), and 1,2-dimethoxyethane (15 cm^3), sealed in a Carius tube, were kept at 50 °C for 48 h. The resulting dark red solution was filtered, evaporated, and a benzene extract of the residue was chromatographed. With diethyl ether–light petroleum (1 : 1) a red solution was eluted affording red *crystals* of $[\mathrm{Ru\{[C(CF_3){:}C(CF_3)]_2C_6H_4PPh_2\}(\eta\text{-}C_5H_5)}]$, (II) (37 mg, 12.4%).

Reactions between $[\mathrm{RuMe(\eta\text{-}C_5H_5)(PPh_3)_2}]$ *and Aromatic Azo-compounds.*—(a) *With azobenzene.* A mixture of the methylruthenium complex (200 mg, 0.28 mmol) and azobenzene (60 mg, 0.33 mmol) was heated under reflux in light petroleum (20 cm^3) for 16 h. The resulting dark green solution was filtered, evaporated to dryness, and a benzene extract was chromatographed. The green fraction eluted with light petroleum–diethyl ether (4 : 1) afforded dark green *crystals* of $[\mathrm{Ru(C_6H_4N{:}NPh)(\eta\text{-}C_5H_5)(PPh_3)}]$, (V; R = H) (65 mg, 38%), identical with an authentic sample.[5b]

(b) *With* m-$\mathrm{RC_6H_4N{:}NPh}$ (R = Me, OMe, CO_2Et, *or* CF_3). Similar reactions carried out with the substituted azo-

TABLE 2

Infrared bands (cm^{-1})[a]

Complex	ν(CO) or ν(C=C)	ν(CC) (fluoroaromatic)	Bands assigned to *o*-disubstituted phenyl-ring vibrations
(I)			1 559, 1 090
(II)	1 647		1 565, 1 103
(IV)			1 076, 830
(V; R = Me) [b]			1 561, 1 092
(V; R = OMe) [b]			1 579, 1 090
(V; R = CO_2Et) [b]	1 702		1 572, 1072
(V; R = CF_3) [b]			1 578, 1 114
(VIa)	1 720		1 573, 1 088
(VIb)	1 714		
(VIII; R = H)		1 509vs	1 574w, 1 094m
(X; R = H)			1 572w, 1 093m
(VIII; R = Me)		1 507vs	1 089m
(X; R = Me)			1 564w, 1 094m
(VIII; R = CF_3)		1 510s	1 600w, 1 092m
(X; R = CF_3)			1 569w, 1 095m
(XI)	1 721, 1 728		
(XII)		1509s	1 093m

[a] Nujol mulls. [b] Isomeric mixtures (see text).

benzenes for 1.5—2 h afforded inseparable mixtures of isomers of the corresponding dark green *ortho*-metallated complexes, (V), obtained in 9 (X = Me), 10.5 (OMe), 9.5 (CO_2Et), and 13% yields (CF_3). The small amounts of product obtained (12—39 mg) precluded a more detailed investigation.

TABLE 3

^{1}H N.m.r. data

Complex	Chemical shift (τ)			Solvent
	Aromatic protons	C_5H_5	Me	
(I)	3.04 (m, br)	5.65 (s)		CS_2
(II)	2.48 (m, br)	4.70 (s)		$CDCl_3$
(III)	2.87 (m)	6.14 (t) [a]		CS_2
(IV)	2.92 (br)	5.74 (t) [b]		$CDCl_3$
(V; R = Me)	2.74 (m), 3.10 (m)	5.10 (s), 5.22 (s) [c]	7.68 (s), 8.22 (s) [c]	$(CD_3)_2CO$
(V; R = OMe)	2.76 (m)	4.41 (s), 5.12 (s), 5.20 (s) [c]	6.11 (s), 6.16 (s), 6.22 (s) [c]	$(CD_3)_2CO$
(V; R = CF_3)	2.80 (m)	4.42 (s), 5.12 (s), 5.15 (s) [c]		$(CD_3)_2CO$
(VIa)	1.15 (s), 1.16 (s), 1.41 (m) (C_6H_3), 1.86 (m), 2.80 (m)	5.16 (s)	6.00 (s)	$CDCl_3$
(VIb)	1.49 (s), 2.33 (s) (C_6H_2), 2.66 (m)	5.03 (s)	6.14 (s), 6.24 (s)	$(CD_3)_2CO$
(VIII; R = H)	2.72 (m, br)	5.33 (s)		$CDCl_3$
(IX; R = H)	2.75 (m)	5.12 (s)		$CDCl_3$
(X; R = H)	2.80 (m, br)	5.12 (s)		$CDCl_3$
(VIII; R = Me)	2.76 (m, br)	5.39 (s)	7.66 (s)	$CDCl_3$
(IX; R = Me)	2.73 (m)	5.14 (s)	7.77 (s)	$CDCl_3$
(X; R = Me)	2.77 (m, br)	5.13 (s)	7.71 (s)	$CDCl_3$
(VIII; R = CF_3)	2.77 (m, br)	5.32 (s)		$CDCl_3$
(IX; R = CF_3)	2.76 (m)	5.08 (s)		$CDCl_3$
(X; R = CF_3)	2.80 (m, br)	5.06 (s)		$CDCl_3$
(XI)	1.23 (m), 1.40 (m), (C_6H_3), 2.76 (m) (PPh_3)	5.01 (s)	6.01 (s)	$CDCl_3$
(XII)	2.90 (m, br)	4.22 (m), 4.42 (m), 4.58 (m), 5.08 (m) [d]		$CDCl_3$
(XIV)	2.75 (m) (PPh_3)	5.44 (s)		$CDCl_3$

[a] J_{HP} 1.5 Hz. [b] J_{HP} 1.0 Hz. [c] Mixtures of isomers (see text). [d] C_5H_4 protons.

(c) *With* 3,5-$(MeCO_2)_2C_6H_3N{:}NPh$. A mixture of the azo-compound (210 mg, 0.71 mmol) and the methylruthenium complex (500 mg, 0.71 mmol) was heated under reflux in light petroleum (40 cm^3) for 4.5 h. Chromatography afforded the following fractions: (*i*) complex (I) [eluted with light petroleum–diethyl ether (9 : 1)] (90 mg, 18.5%); (*ii*) unchanged azo-compound [light petroleum–diethyl ether (4 : 1)] dark green (90 mg, 43%); (*iii*) $[Ru\{C_6H_4N{:}NC_6H_3(CO_2Me)_2\}(\eta\text{-}C_5H_5)(PPh_3)]$, (VIa) [light petroleum—diethyl ether (3 : 2)] (30 mg, 10%); and (*iv*) $[Ru\{C_6H_2(CO_2Me)_2N{:}NPh\}(\eta\text{-}C_5H_5)(PPh_3)]$, (VIb) [light petroleum–diethyl ether (1 : 9)] dark green (21 mg, 7%).

(d) *With* $PhN{:}NC_6F_5$. A similar reaction between $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ (500 mg, 0.71 mmol) and pentafluoroazobenzene (200 mg, 0.74 mmol) afforded, on chromatography, unchanged $PhN{:}NC_6F_5$ (eluted with light petroleum) (107 mg, 53.5%), light green *crystals* of $[Ru(C_6H_4N{:}NC_6F_5)(\eta\text{-}C_5H_5)(PPh_3)]$, (VIII; R = H) [eluted with light petroleum–diethyl ether (1 : 19), and crystallised from light petroleum] (44 mg, 19%), dark green *crystals* of $[Ru(C_6F_4N{:}NPh)(\eta\text{-}C_5H_5)(PPh_3)]$, (IX; R = H) [light petroleum–diethyl ether (9 : 1), crystallised from light petroleum–diethyl ether)] (35 mg, 15.5%), and finally dark green *crystals* of $[Ru(C_6F_4N{:}NC_6H_4C_6H_4PPh_2)(\eta\text{-}C_5H_5)]$ (X; R = H) [in a brown band obtained with light petroleum–

TABLE 4

^{19}F N.m.r. data

Complex	Chemical shift (p.p.m.) [a]					Coupling constant (Hz)						Solvent
	CF_3	$F^{2,6}$	F^3	F^4	F^5	$J(F^2F^3)$	$J(F^2F^4)$	$J(F^2F^5)$	$J(F^3F^4)$	$J(F^3F^5)$	$J(F^4F^5)$	
(V; R = CF_3) [b]	60.75 (s), 61.20 (s) 61.75 (s)											$(CD_3)_2CO$
(VIII; R = H)		148.8	163.8	160.7	163.8		0		21.5			$CDCl_3$
(IX; R = H)		142.1	168.0	158.8	118.0	19.6	0	16.4	19.4	2.6	30.2	$CDCl_3$
(X; R = H)		142.7	167.5	158.3	117.9	18.8	0	16.7	19.8	0	30.2	$CDCl_3$
(VIII; R = Me)		148.1	163.1	159.9	163.1		0		21.1			$CDCl_3$
(IX; R = Me)		142.1	167.9	158.8	118.2	19.6	0	16.7	19.4	2.5	30.6	$CDCl_3$
(X; R = Me)		142.2	167.5	158.4	118.2	19.4	0	16.7	19.6	2.0	30.2	$CDCl_3$
(VIII; R = CF_3)		148.05	162.6	158.7	162.6		0		21.1			$CDCl_3$
(IX; R = CF_3)	62.3 (s)	141.3	167.2	157.7	117.7	19.6	2.0	17.0	19.8	2.4	29.2	$CDCl_3$
(X; R = CF_3)	62.86 (s)	141.9	166.9	157.3	117.6	18.9	0	18.0	19.3	2.0	30.5	$CDCl_3$
(XI)		140.8	167.2	157.6	117.5	20.0	1.9	17.2	19.3	2.2	29.9	$CDCl_3$
(XII) C_6F_5		147.9	162.3	158.6	162.3		0		21.0			$CDCl_3$
(XII) C_6F_4		142.5	167.1	156.7	115.8	18.2	0	17.9	18.8	0	29.2	

[a] Relative to CCl_3F (0.00 p.p.m.). [b] Mixture of isomers.

diethyl ether (3 : 1), and recrystallised from light petroleum–dichloromethane] (20 mg, 9%).

(e) *With* m-$RC_6H_4N{:}NC_6F_5$ (R = Me *or* CF_3). Similar reactions with the substituted pentafluoroazo-compounds afforded related complexes, which were chromatographed with light petroleum–diethyl ether. So obtained from *m*-$MeC_6H_4N{:}NC_6F_5$ were (VIII) (53 mg, 11.5%), (IX) (34 mg, 9%), and (X; R = Me) (23 mg, 6%), together with unchanged azo-compound (162 mg, 52%), while *m*-F_3C-$C_6H_4N{:}NC_6F_5$ afforded (VIII) (60 mg, 16%), (IX) (52 mg, 9%), and (X; R = CF_3) (22 mg, 6%), with unchanged azo-compound (131 mg, 44%).

(f) *With* 3,5-$(MeCO_2)_2C_6H_3N{:}NC_6F_5$. The reaction between $[RuMe(\eta\text{-}C_5H_5)(PPh_3)_2]$ (1 150 mg, 1.6 mmol) and 3,5-$(MeCO_2)_2C_6H_3N{:}NC_6F_5$ (620 mg, 1.6 mmol) in refluxing light petroleum for 4.5 h afforded the green *complex* $[\overline{\mathrm{Ru}\{C_6F_4N{:}N}C_6H_3(CO_2Me)_2\}(\eta\text{-}C_5H_5)(PPh_3)]$, (XI) (145 mg, 21%), together with unchanged azo-compound (252 mg, 40.5%).

(g) *With* $C_6F_5N{:}NC_6F_5$. Using decafluoroazobenzene (320 mg, 0.91 mmol) and the methyl complex (600 mg, 0.85 mmol) in a similar reaction for 2.5 h gave unchanged $C_6F_5N{:}NC_6F_5$ (105 mg, 33%) (eluted with light petroleum) and complex (XII) (200 mg, 54%), eluted with light petroleum–diethyl ether (9 : 1).

Preparation of $[Ru(\eta\text{-}C_5H_5)F(PPh_3)_2]$.—The complex $[Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2]$ (500 mg, 0.69 mmol) was added to a saturated solution of $[NH_4]F$ in methanol (50 cm^3). The mixture was boiled briefly, and silver(I) carbonate (200 mg, 0.74 mmol) was added. Filtration into 0.1M-aqueous $[NH_4]F$ resulted in precipitation of a pale yellow solid, which on careful recrystallisation from methanol afforded $[Ru(\eta\text{-}C_5H_5)F(PPh_3)_2]$, (XIV) (251 mg, 51.6%).

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