Metallation of Azobenzenes by Fluorine-abstraction: Structure of a Ruthenium Complex Containing Nonafluoro(phenylazo)phenyl-2*C*,*N*′ and Diphenyl-2-(η-cyclopentadienylphenyl)phosphine Groups

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Summary The formation of metallated azobenzene derivatives by fluorine-abstraction reactions using nucleophilic transition metal reagents has been achieved; the structure of an *ortho*-metallated complex, derived from decafluoroazobenzene and also containing a $Ph_2P(C_6H_4\text{-}C_5H_4)$ ligand is described.

Formation of *ortho*-metallated derivatives of azobenzenes has involved loss of a hydrogen atom from an aromatic ring as molecular hydrogen, methane, or hydrogen chloride.[1] With palladium(II) chloride evidence for an electrophilic reaction has been generally accepted.[2] However, electron-rich transition metal complexes appear to metallate azobenzenes by a nucleophilic mechanism.[3] Since fluorocarbons, particularly polyfluoroaromatic compounds, are particularly susceptible to nucleophilic attack it seemed possible that penta- and deca-fluoroazobenzene could be metallated by loss of fluoride, establishing a new reaction path for the formation of carbon–metal σ-bonds by *ortho*-metallation.

The ruthenium compound $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$, which is very prone to form metallated complexes,[4] reacts with decafluoroazobenzene in light petroleum at 100° to afford dark green $\overline{\mathrm{RuC_6F_4N:N}}\mathrm{C_6F_5(Ph_2PC_6H_4\text{-}\eta\text{-}C_5H_4)}$, m.p. 116° [*M*, 770 ^{19}F n.m.r., (CCl_3F) 115·8, 142·5, 156·7, and 167·1 (1:1:1:1, C_6F_4), and 147·9, 158·6, 162·3 p.p.m. (2:1:2, C_6F_5)]. The ^1H n.m.r. spectrum contained four multiplets at τ 4·22, 4·44, 4·58, and 5·09, all of equal intensity, but not the sharp singlet expected for the $\eta\text{-}C_5H_5$ group. These data are consistent with an unusual structure, established by a single crystal *X*-ray diffraction study (Figure), in which substitution of both a C_6F_5 and an $\eta\text{-}C_5H_5$ ring has occurred.

Crystals of diphenyl-2-(η-cyclopentadienylphenyl)phosphinenonafluoro(phenylazo)phenyl-2*C*,*N*′-ruthenium are monoclinic, space group $P2_1/c$, with $a = 15{\cdot}650\ (14)$, $b = 13{\cdot}338(11)$, $c = 14{\cdot}741(11)$ Å, $\beta = 97{\cdot}38(3)°$. Calculated ($Z = 4$) and observed densities are 1·68 and 1·71(3) g/cm^3 respectively. The structure analysis was based upon 3092 independent nonzero intensities collected by the (θ-2θ) scan technique on a Picker diffractometer. Solution of the structure was achieved by Patterson and Fourier methods. Full-matrix isotropic least-squares refinement, in which the three phenyl rings were treated as groups, converged to a conventional *R* factor of 0·075.

The co-ordination geometry is of the familiar $(\eta\text{-}C_5H_5)\text{-}ML_3$ type, distorted somewhat by the constraints of the chelate rings. The metallated nonafluoro(phenylazo)phenyl ligand is nonplanar, with the free pentafluorophenyl ring twisted by 64·2° from the Ru–Cl–C(6)–N(1)–N(2) plane.

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Bond distances involving this ligand include Ru–C(1) = 2·018(10) Å, Ru–N(2) = 2·014(8) Å, and N(1)–N(2) = 1·324(11) Å. Linkage of the cyclopentadienyl carbon atom C(17) with the phenyl carbon C(19) forms a σ, π-chelating arrangement of the sort previously observed in two iron carbonyl complexes.[5] The C_5H_4 ring is nearly perpendicular (dihedral angle = 91·0°) to the phenyl ring to which it is bound. Distances within the substituted cyclopentadienyl ring are equal within experimental error; however C(13) and C(17) are somewhat closer to the metal atom [mean Ru–C distance = 2·190(11) Å] than are the other three ring carbon atoms [mean Ru–C distance = 2·248(12) Å]. Other distances involving this ligand include Ru–P = 2·283(3) Å, P–C(18) = 1·803(7) Å and C(17)–C(19) = 1·472(12) Å.

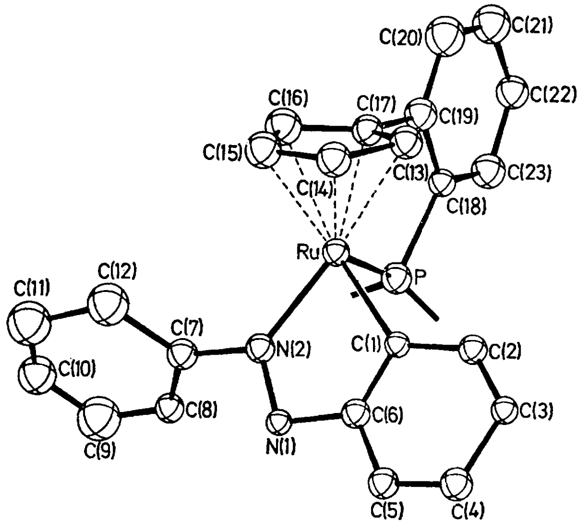

FIGURE. The molecular structure of $RuC_6F_4N:NC_6F_5$ ($Ph_2PC_6H_4$-η-C_5H_4). Fluorine atoms have been omitted for clarity.

Reaction between pentafluoroazobenzene and decacarbonyldimanganese affords two complexes in low yields, readily identified as compounds in which the C_6F_5- and C_6H_5-rings, respectively, have been metallated; $MnC_6F_4N:N$-$Ph(CO)_4$, m.p. 145—148°, [*M*, 420, ^{19}F n.m.r., 115, 138, 149, and 162 p.p.m., (1 : 1 : 1 : 1)]; $MnC_6H_4N:NC_6F_5(CO)_4$ m.p. 77—79°, [*M*, 438, ^{19}F n.m.r. 150·5, 155·0, 161·0 p.p.m., (2 : 1 : 2)]. Pentafluoroazobenzene and palladium chloride react to give only $(ClPdC_6H_4N:NC_6F_5)_2$.

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