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Metallation of Azobenzenes by Fluorine-abstraction: Structure of a Ruthenium Complex Containing Nonafluoro(phenylazo)phenyl-2C,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 $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-C}_6\text{H}_5)$ 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 $\text{RuMe}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$, which is very prone to form metallated complexes,⁴ reacts with decafluoroazobenzene in light petroleum at 100° to afford dark green $\text{RuC}_6\text{F}_4\text{N}:\text{NC}_6\text{F}_5(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}\eta\text{-C}_5\text{H}_5)$, 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 $\eta\text{-C}_5\text{H}_5$ 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 $\eta\text{-C}_5\text{H}_5$ ring has occurred.

Crystals of diphenyl-2-(η -cyclopentadienylphenyl)phosphinenonafluoro(phenylazo)phenyl-2C,N'-ruthenium are monoclinic, space group $P2_1/c$, with $a = 15.650$ (14), $b = 13.338$ (11), $c = 14.741$ (11) Å, $\beta = 97.38$ (3)°. Calculated ($Z = 4$) and observed densities are 1.68 and 1.71 (3) g/cm³ respectively. The structure analysis was based upon 3092 independent nonzero intensities collected by the (θ -2 θ) 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 ($\eta\text{-C}_5\text{H}_5$)- 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 $\text{Ru-Cl-C(6)-N(1)-N(2)}$ 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 arrange-

FIGURE. The molecular structure of $\text{RuC}_6\text{F}_4\text{N}:\text{NC}_6\text{F}_5(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}\eta\text{-C}_5\text{H}_5)$. Fluorine atoms have been omitted for clarity.

ment 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.

Reaction between pentafluoroazobenzene and decacarbonyldimanganese affords two complexes in low yields, readily identified as compounds in which the $\text{C}_6\text{F}_5\text{-}$ and $\text{C}_6\text{H}_5\text{-}$ rings, respectively, have been metallated; $\text{MnC}_6\text{F}_4\text{N}:\text{N-Ph}(\text{CO})_4$, m.p. $145\text{--}148^\circ$, [M , 420, ^{19}F n.m.r., 115, 138, 149, and 162 p.p.m., (1:1:1:1)]; $\text{MnC}_6\text{H}_4\text{N}:\text{NC}_6\text{F}_5(\text{CO})_4$, m.p. $77\text{--}79^\circ$, [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 $(\text{ClPdC}_6\text{H}_4\text{N}:\text{NC}_6\text{F}_5)_2$.

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