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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 Ph₂P(η-C₅H₅) 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 fluoro-carbons, particularly polyfluoroaromatic compounds, are particularly susceptible to nucleophilic attack it seemed possible that penta- and deca-fluorazoobenzene could be metallated by loss of fluoride, establishing a new reaction path for the formation of carbon-metal o-bonds by ortho-metallation.

The ruthenium compound RuMe(PP₃)₄(η-C₆H₆), which is very prone to form metallated complexes,⁴ reacts with decafluoroazobenzene in light petroleum at 100° to afford dark green Ru₄F₄N:NC₄F₃(Ph₂PC₅H₅-η-C₆H₆), m.p. 116° [M, 770 (3) n.m.r., (CCl₄)F 115-8, 142-5, 156-7, and 167-1 (1:1:1:1, C₄F₂), and 147-9, 158-6, 162-3 p.p.m. (2:1:2, C₄F₂)]. The ¹H n.m.r. spectrum contained four multiplets at 4.22, 4.44, 4.58, and 5.09, all of equal intensity, but not the sharp singlet expected for the η₆-C₆H₆ 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 C₄F₃ and an η₆-C₆H₆ ring has occurred.

Crystals of diphenyl-2-(η-cyclopentadienylphenyl)phosphinenonafluoro(phenylazo)phenyl-2C,N'-ruthenium are monoclinic, space group P2₁/c, with a = 15-660 (14), b = 13-336 (11), c = 14-741 (11) Å, β = 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-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 (η₆-C₆H₆)-ML₄ 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(l) = 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. The C₅H₄ ring is nearly perpendicular (dihedral angle = 91°) 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(l8) = 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 C₅F₅- and C₅H₅-rings, respectively, have been metallated; MnC₅F₅N: N-Ph(CO)₄, m.p. 145–148°, [M, 420, ¹⁹F n.m.r., 115, 138, 149, and 162 p.p.m., (1:1:1:1)]; MnC₅H₅N: NC₅F₅(CO)₄ m.p. 77–79°, [M, 438, ¹⁹F n.m.r. 150.5, 155.0, 161.0 p.p.m., (2:1:2)]. Pentafluoroazobenzene and palladium chloride react to give only (ClPd(C₅H₅N): NC₅F₅)₄.

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