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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(C₆H₄-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 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(PPh₃)₂(η -C₅H₅), which is very prone to form metallated complexes,⁴ reacts with decafluoroazobenzene in light petroleum at 100° to afford dark green $\text{RuC}_6\text{F}_4\text{N}:\text{NC}_6\text{F}_5(\text{Ph}_2\text{PC}_6\text{H}_4-\eta\text{-C}_5\text{H}_5)$, m.p. 116°

[*M*, 770 ¹⁹F n.m.r., (CCl₃F) 115·8, 142·5, 156·7, and 167·1 (1:1:1:1, C₆F₄), and 147·9, 158·6, 162·3 p.p.m. (2:1:2, C₆F₅)]. 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 η -C₅H₅ 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 C₆F₅ and an η -C₅H₅ ring has occurred.

Crystals of diphenyl-2-(η -cyclopentadienylphenyl)phosphenonafluoro(phenylazo)phenyl-2C,N'-ruthenium are monoclinic, space group *P*2₁/*c*, with *a* = 15·650 (14), *b* = 13·338(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 -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 (η -C₅H₅)-ML₃ 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 arrange-

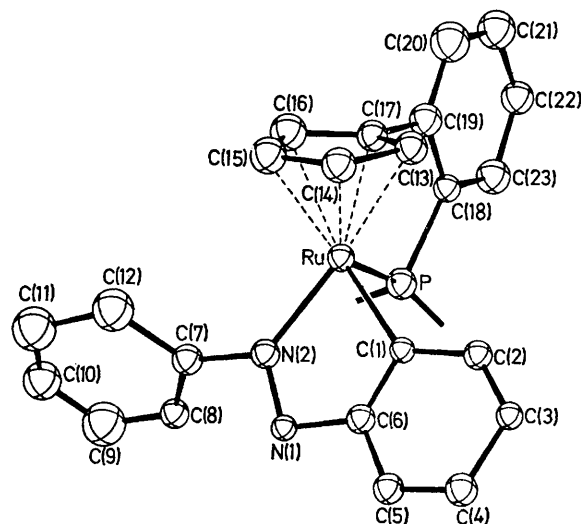


FIGURE. The molecular structure of $\text{RuC}_6\text{F}_4\text{N}:\text{NC}_6\text{F}_5(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}\eta\text{-C}_6\text{H}_5)$. Fluorine atoms have been omitted for clarity.

- ¹ M. I. Bruce and B. L. Goodall, in 'The Chemistry of Hydrazo, Azo and Azoxy Groups,' ed S. Patai, Wiley, New York, in the press.
² G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.
³ M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 558.
⁴ M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **40**, C39.
⁵ L. F. Dahl, R. J. Doedens, W. Hubel, and J. Nielsen, *J. Amer. Chem. Soc.*, 1966, **88**, 446; P. J. Van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *ibid.*, 1971, **93**, 4394.

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 C_6F_5 - and C_6H_5 -rings, respectively, have been metallated; $\text{MnC}_6\text{F}_4\text{N}:\text{N-Ph}(\text{CO})_4$, m.p. 145–148°, [*M*, 420, ¹⁹F 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. 77–79°, [*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 $(\text{ClPdC}_6\text{H}_4\text{N}:\text{NC}_6\text{F}_5)_2$.

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