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Crystal and Molecular Structure of a Ruthenium Complex Containing a Metalated Perfluoroazobenzene Ligand and a Novel 2-(η-Cyclopentadienyl)phenyl Group

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The product of the reaction of decafluoroazobenzene with $Ru(CH_3)(PPh_3)_2(\eta\text{-}C_5H_5)$ has been shown by a crystal structure analysis to have an unusual structure. Crystals of (diphenyl(2-(η-cyclopentadienyl)phenyl)phosphine)(nonafluoro-(phenylazo)phenyl-C^2,N')ruthenium are monoclinic, space group $P2_1/c$, with four molecules in a unit cell of dimensions a = 15.650 (14) Å, b = 13.338 (11) Å, c = 14.741 (11) Å, and β = 97.38 (3)°. The structure determination was based upon 3092 independent nonzero diffraction maxima with $2\theta < 45°$ collected by counter methods. A blocked full-matrix least-squares refinement converged to a final conventional discrepancy factor of 0.046. The molecule contains not only the expected metalated perfluoroazobenzene ligand but also a linkage between the η-cyclopentadienyl group and one of the phenyl rings of the triphenylphosphine. The resulting σ,π chelating configuration causes the substituted cyclopentadienyl ring to be tilted by ~13° relative to the ML_3 portion of the molecule. The fluorinated azobenzene ligand is bound in a chelating fashion via Ru–C and Ru–N bonds. The free phenyl ring is twisted by 64.6° from from the chelate plane. Bond distances involving this ligand include Ru–N = 2.020 (5) Å, Ru–C = 2.013 (6) Å, and N–N = 1.310 (7) Å.

Introduction

The ortho metalation of azobenzene, first reported about 10 years ago,[1] has proven to be the prototype of an extensive and important series of chemical reactions.[2-4] These reactions typically involve formation of a metal–carbon σ bond to an aromatic ring, with the displaced hydrogen atom either being eliminated or remaining bound to the metal atom. It is generally believed that the metalation of azobenzene proceeds by a pathway involving initial metal coordination of the azo group, followed by intramolecular attack upon the aromatic ring remote from the bound nitrogen atom.[2] Studies of the metalation of substituted azobenzenes by $PdCl_4^{2-}$ strongly suggested an electrophilic mechanism for the intramolecular metalation process in this case.[5,6] However, it has been suggested that under other circumstances (e.g., electron-rich metal atoms, azobenzenes with electron-withdrawing substituents) metalation could occur by a nucleophilic pathway.[7] This hypothesis has found support in studies of the metalation reaction of 3-monofluoroazobenzene with $CH_3Mn(CO)_5$, where the predominant product is the isomer which would be favored by a nucleophilic mechanism.[6]

In view of these results, the reactions of polyfluorinated azobenzenes, which should be susceptible to nucleophilic attack, with various transition metal systems have been investigated[8,9] in order to determine whether metalation can occur by fluorine abstraction from these ligands. From the reaction of $Ru(CH_3)(PPh_3)_2(\eta\text{-}C_5H_5)$ with decafluoroazobenzene, a product was obtained whose ^{19}F NMR spectrum was that expected of a metalated $C_6F_5N_2C_6F_4$ ligand but whose ^1H NMR spectrum suggested that substitution had also occurred on the cyclopentadienyl ring.[9] We now report results of a crystal structure analysis of this product, which confirms the proposed metalated structure and demonstrates that an unusual type of linkage has been formed between the cyclopentadienyl group and one of the phenyl rings of the triphenylphosphine ligand. These results have previously appeared in preliminary form.[10]

Table I

	A. Crystal Data		
Formula	$RuC_{35}F_9H_{18}N_2P$	V	3051.5 Å^3
Fw	769.57	Z	4
a	15.650 (14)Å	d(obsd)	1.70 (5) g/cm^3
b	13.338 (11) Å	d(calcd)	1.68 g/cm^3
c	14.741 (11) Å	Space group	$P2_1/c$
β	97.38 (3)°	μ(Mo Kα)	6.5 cm^{-1}
	B. Experimental Parameters		
Radiation	Mo Kα, λ(Kα_1) 0.709 30 Å, 3.0-mil Nb filter	Scan range	−0.65 + 0.60° in 2θ from Kα_1 peak
Temp	23 °C	Background counting	20-s fixed counts at each end of scan
Receiving aperture	5 × 5 mm, 29 cm from crystal		
Takeoff angle	2.1°	2θ(max)	45°
		Data collected	4135
Scan rate	1.0°/min in 2θ	Data with $F_o^2 > 3\sigma(F_o^2)$	3092

Experimental Section

Data Collection and Reduction. A suitably crystalline sample of the title compound was supplied by Dr. M. I. Bruce. Preliminary precession photographs showed monoclinic symmetry with systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) uniquely defining space group $P2_1/c$. Cell parameters were obtained by least-squares refinement of the setting angles of 13 reflections which had been accurately centered on a Picker four-circle x-ray diffractometer.[11] Owing to the solubility of the crystals in many solvents and to the limited amount of sample available, only an approximate value of the observed density could be determined by flotation methods. Crystal data are tabulated in part A of Table I.

Intensity data were collected from a dark green thin platelet of dimensions 0.09 × 0.23 × 0.38 mm mounted approximately along the crystallographic b axis. Bounding planes belonged to the {100}, {010}, {001}, and {110} forms. Narrow-source, open-counter ω scans through several reflections displayed an average full width at half-

Table II. Positional, Thermal, and Group[c] Parameters for $Ru(C_6F_4N_2C_6F_5)(Ph_2PC_6H_4\text{-}\eta\text{-}C_5H_4)$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	−0.220 77 (3)[a]	0.054 92 (3)	0.223 30 (3)	37.2 (3)[b]	42.3 (4)	38.2 (3)	4.5 (2)	5.9 (19)	0.8 (2)
P	−0.244 92 (10)	−0.025 52 (11)	0.354 37 (11)	36.7 (8)	42.1 (10)	42.1 (9)	1.1 (7)	6.0 (7)	1.4 (7)
N1	−0.307 7 (3)	0.243 5 (4)	0.257 1 (3)	41 (3)	48 (4)	48 (3)	6 (2)	4 (2)	−1 (3)
N2	−0.318 0 (3)	0.155 2 (4)	0.218 3 (4)	35 (3)	53 (4)	49 (3)	4 (2)	−2 (2)	−2 (3)
C1	−0.168 0 (4)	0.174 3 (4)	0.292 9 (4)	34 (3)	52 (4)	33 (3)	4 (3)	6 (2)	6 (3)
C2	−0.086 2 (4)	0.191 3 (5)	0.337 7 (4)	36 (3)	51 (4)	46 (4)	8 (3)	6 (3)	11 (3)
C3	−0.061 8 (4)	0.279 2 (5)	0.379 0 (4)	45 (4)	58 (5)	40 (4)	−13 (3)	2 (3)	5 (3)
C4	−0.118 2 (5)	0.357 2 (5)	0.376 9 (4)	63 (4)	40 (4)	42 (4)	−8 (4)	7 (3)	−2 (30)
C5	−0.199 9 (4)	0.346 6 (4)	0.337 7 (5)	46 (4)	41 (4)	56 (4)	7 (3)	3 (3)	2 (3)
C6	−0.224 5 (4)	0.255 9 (4)	0.296 2 (4)	38 (3)	47 (4)	37 (3)	4 (3)	3 (3)	5 (3)
C7	−0.407 0 (4)	0.139 6 (5)	0.185 0 (5)	36 (3)	50 (4)	61 (4)	6 (3)	−3 (3)	3 (3)
C8	−0.469 2 (5)	0.141 2 (5)	0.242 1 (6)	44 (4)	58 (5)	70 (5)	4 (3)	4 (4)	8 (4)
C9	−0.555 4 (5)	0.129 7 (6)	0.209 9 (8)	40 (4)	72 (6)	12 (8)	2 (4)	2 (5)	2 (5)
C10	−0.579 6 (5)	0.115 2 (6)	0.119 9 (8)	39 (4)	78 (6)	119 (8)	0 (4)	−16 (5)	−7 (6)
C11	−0.520 4 (6)	0.116 8 (6)	0.062 2 (6)	60 (5)	74 (6)	85 (6)	6 (4)	−19 (5)	−24 (5)
C12	−0.434 6 (4)	0.129 0 (5)	0.093 5 (6)	36 (4)	67 (5)	75 (5)	6 (3)	−7 (4)	−8 (4)
F1	−0.026 3 (2)	0.117 8 (3)	0.343 2 (3)	42 (2)	67 (3)	82 (3)	7 (2)	−2 (2)	1 (2)
F2	0.019 2 (3)	0.291 5 (3)	0.421 1 (3)	55 (2)	94 (3)	74 (3)	−17 (2)	−11 (2)	−5 (2)
F3	−0.090 1 (3)	0.445 3 (3)	0.416 8 (3)	77 (2)	62 (3)	67 (2)	−16 (2)	6 (2)	−14 (2)
F4	−0.255 9 (3)	0.422 6 (3)	0.338 1 (3)	77 (2)	58 (3)	96 (3)	17 (2)	8 (2)	−16 (2)
F5	−0.447 0 (3)	0.153 4 (3)	0.331 8 (3)	59 (2)	107 (4)	77 (3)	12 (2)	21 (2)	11 (3)
F6	−0.612 7 (3)	0.128 9 (5)	0.270 3 (5)	53 (2)	156 (5)	163 (5)	2 (3)	33 (3)	18 (4)
F7	−0.663 4 (3)	0.105 1 (4)	0.089 2 (4)	46 (2)	138 (5)	184 (6)	−4 (3)	−24 (3)	16 (4)
F8	−0.544 6 (3)	0.109 4 (4)	−0.029 0 (4)	80 (3)	150 (5)	104 (4)	18 (3)	−38 (3)	−40 (4)
F9	−0.379 4 (3)	0.135 5 (4)	0.032 0 (3)	66 (2)	134 (4)	63 (3)	15 (3)	−7 (2)	−9 (3)
C13	−0.104 7 (4)	−0.019 5 (5)	0.187 3 (4)	46 (3)	52 (4)	54 (4)	8 (3)	18 (3)	2 (3)
C14	−0.135 8 (5)	0.043 9 (5)	0.114 5 (5)	64 (4)	58 (5)	56 (4)	6 (4)	25 (4)	3 (4)
C15	−0.217 5 (6)	0.009 3 (6)	0.077 7 (5)	78 (5)	71 (5)	43 (4)	19 (4)	13 (4)	2 (4)
C16	−0.238 6 (5)	−0.076 5 (5)	0.125 8 (5)	56 (4)	65 (5)	48 (4)	7 (4)	8 (3)	−16 (4)
C17	−0.168 4 (4)	−0.092 2 (5)	0.196 2 (4)	45 (3)	47 (4)	54 (4)	12 (3)	16 (3)	−3 (3)

Group	x_0	y_0	z_0	ϕ, deg	θ, deg	ρ, deg
Ring 1	−0.157 58 (18)	−0.239 78 (22)	0.338 47 (20)	−156.55 (16)	169.10 (12)	−104.39 (15)
Ring 2	−0.437 96 (20)	−0.093 73 (22)	0.378 40 (22)	107.17 (16)	−167.84 (12)	−88.02 (18)
Ring 3	−0.167 18 (19)	0.094 46 (21)	0.533 69 (19)	−35.79 (17)	−134.02 (15)	−177.87 (18)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Tabulated β values are × 10^4. [c] The coordinates x_0, y_0, and z_0 are the fractional coordinates of the origin of the group coordinate system (taken at the midpoint of the ring); the angles ϕ, θ, and ρ are the orientation angles defined by R. J. Doedens in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 198–200.

maximum of 0.15°, indicative of a satisfactorily low mosaic spread. Intensity data were collected on a Picker automatic diffractometer by use of procedures previously described.[12] Experimental parameters specific to this data set are summarized in part B of Table I. No reflections required attenuation to bring their peak intensities within the linear range of the counting system. Four standard reflections, chosen from widely different regions of reciprocal space, were monitored every 100 reflections throughout the data collection. The intensities of these reflections varied less than ±3% and showed no systematic deviations. The intensity data were processed according to previously described methods.[12] The p factor in the expression for the standard deviation of the observed intensities was assigned a value of 0.05. A trial calculation indicated that transmission factors ranged only from 0.92 to 0.97; hence no absorption correction was applied.

Solution and Refinement of the Structure. Solution of the structure was achieved by heavy-atom Patterson and difference Fourier methods. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms, based upon all data with $F_o^2 \geq 3\sigma(F_o)^2$, converged to discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.075$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.096$. The phenyl rings of the triphenylphosphine ligand were treated as rigid groups with the hydrogen atoms included in the groups (C–C = 1.39 Å, C–C–C = H–C–C = 120°, C–H = 0.95 Å). Further refinement employed anisotropic temperature factors for all nonhydrogen atoms other than the group atoms. Hydrogen atoms for the cyclopentadienyl ring were included as fixed contributions to F_c based upon their "ideal" trigonal positions. The anisotropic refinement was carried out in blocks because of the number of parameters involved. The first block included the scale factor, the metal atom, and the substituted azobenzene ligand. The remaining atoms and groups together with the scale factor and the Ru atom comprised the second block. The blocks were refined alternately and new hydrogen atom positions were calculated for the cyclopentadienyl ring after each pair of cycles. This final refinement converged to $R_1 = 0.046$ and $R_2 = 0.058$, with the largest parameter shift in the last cycle equal to 1.3σ. The largest peak (1.1 e Å^{-3}) on a final difference map at this point was very close to F7 and apparently represented residual motion of that atom not accounted for in the thermal model.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The final standard deviation of an observation of unit weight was 1.5. Calculation of $w(\Delta F)^2$ for subsets of the data as a function of uncorrected intensity, observed F, and Bragg angle showed no significant trends, thus confirming that the relative weights were appropriate. Calculation of structure factors for data with $F_o^2 \leq 3\sigma F_o^2$ revealed 12 reflections with $(|F_o| - |F_c|)/\sigma(F_o) \geq 3$; only three of these had $\Delta F/\sigma > 4$. Scattering factors for Ru, P, and F were those of Cromer and Waber,[13] those for C and N were taken from ref 14, and those of Stewart et al.[15] were employed for H. Structure factor calculations used the $\Delta f'$ and $\Delta f''$ values of Cromer[16] in estimating the real and imaginary parts of anomalous scattering by the Ru and P atoms.

Final atomic positional and thermal parameters for the nongroup atoms are listed in Table II. Positional and thermal parameters for the group and hydrogen atoms are given in Table III. Intramolecular distances and angles are tabulated in Tables IV and V. The principal root-mean-square amplitudes of thermal motion for the atoms refined anisotropically are listed in Table VI.[17] Information concerning selected molecular planes and dihedral angles is given in Table VII. A table of observed and calculated structure factors is available.[17]

Description of the Structure and Discussion

An overall view of the molecular structure of (diphenyl(2-(η-cyclopentadienyl)phenyl)phosphine)(nonafluoro(phenylazo)phenyl-C^2,N')ruthenium is shown in Figure 1. As suggested on the basis of ^{19}F and ^1H NMR spectra, the

Table III. Atomic Positions of Group Atoms and Hydrogen Atoms

	x	*y*	*z*	*B*, Å^2
		Ring 1		
C18	−0.1926 (3)[a]	−0.1458 (2)	0.3515 (3)	3.43 (11)
C19	−0.1631 (3)	−0.1687 (3)	0.2689 (2)	3.84 (12)
C20	−0.1280 (3)	−0.2627 (3)	0.2558 (2)	5.77 (17)
C21	−0.1225 (3)	−0.3338 (3)	0.3254 (3)	6.39 (18)
C22	−0.1521 (3)	−0.3109 (3)	0.4080 (3)	5.06 (15)
C23	−0.1871 (3)	−0.2169 (3)	0.4211 (2)	4.46 (14)
H20[b]	−0.1078 (4)	−0.2783 (5)	0.1994 (3)	*c*
H21	−0.0986 (4)	−0.3980 (3)	0.3165 (4)	
H22	−0.1484 (5)	−0.3595 (4)	0.4556 (3)	
H23	−0.2073 (4)	−0.2013 (4)	0.4776 (3)	
		Ring 2		
C24	−0.3542 (2)	−0.0636 (3)	0.3699 (3)	3.99 (12)
C25	−0.3797 (3)	−0.0760 (4)	0.4563 (2)	5.42 (16)
C26	−0.4634 (3)	−0.1062 (4)	0.4647 (3)	6.63 (19)
C27	−0.5217 (2)	−0.1238 (4)	0.3869 (3)	6.61 (19)
C28	−0.4963 (3)	−0.1114 (4)	0.3005 (3)	5.78 (17)
C29	−0.4125 (3)	−0.0813 (3)	0.2921 (2)	4.78 (14)
H25	−0.3399 (4)	−0.0640 (6)	0.5095 (3)	
H26	−0.4808 (4)	−0.1146 (6)	0.5237 (3)	
H27	−0.5789 (3)	−0.1444 (6)	0.3926 (5)	
H28	−0.5361 (3)	−0.1235 (6)	0.2473 (3)	
H29	−0.3951 (4)	−0.0728 (5)	0.2331 (2)	
		Ring 3		
C30	−0.2036 (2)	0.0356 (3)	0.4608 (2)	3.45 (12)
C31	−0.1237 (3)	0.0103 (3)	0.5078 (3)	4.46 (13)
C32	−0.0872 (2)	0.0691 (4)	0.5807 (3)	5.52 (16)
C33	−0.1307 (3)	0.1533 (3)	0.6066 (3)	5.69 (17)
C34	−0.2107 (3)	0.1786 (3)	0.5596 (3)	5.19 (15)
C35	−0.2471 (2)	0.1198 (4)	0.4867 (3)	3.93 (13)
H31	−0.0940 (4)	−0.0472 (5)	0.4901 (4)	
H32	−0.0326 (3)	0.0518 (6)	0.6127 (4)	
H33	−0.1059 (4)	0.1934 (4)	0.6563 (4)	
H34	−0.2404 (5)	0.2361 (5)	0.5773 (4)	
H35	−0.3017 (3)	0.1371 (6)	0.4546 (4)	
		Cyclopentadienyl Hydrogen Atoms		
H13	−0.0503	−0.0144	0.2440	
H14	−0.1067	0.1003	0.0938	
H15	−0.2531	0.0391	0.0280	
H16	−0.2893	−0.1160	0.1138	

[a] Standard deviations of group atomic coordinates are estimated from the errors of the group parameters and may be meaningfully used only to estimate errors in distances between group and nongroup atoms or between atoms in *different* groups. [b] The numbering of the hydrogen atoms corresponds to that of the carbon atoms; e.g., H(2) is bound to C(2), etc. [c] Hydrogen atoms were assigned thermal parameters one unit greater than those of the corresponding carbon atoms.

molecule contains not only the expected metalated perfluoroazobenzene ligand but also an unusual linkage between the η-cyclopentadienyl group and one of the phenyl rings of the triphenylphosphine. This intramolecular linkage results in a σ,π-chelating configuration analogous to that previously found in two dicarbonyliron complexes. One of these, $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$, contains an oxy-$\sigma$-vinyl grouping which bridges from an iron atom to a substituted η-cyclopentadienyl ligand.[18] In the other iron complex, of stoichiometry $C_8H_8COFe(CO)_2$, a σ-propenoyl group links a η-cyclohexadienyl ligand to the iron atom.[19]

The configuration about the ruthenium atom is of the familiar η-$(C_5H_5)ML_3$ type, distorted somewhat by the constraints of the chelate rings. The major distortions from ideal "piano-stool" geometry are related to the 75.6 (2)° bite angle of the nonafluoro(phenylazo)phenyl ligand and to a small tilting of the plane of the cyclopentadienyl group relative to the ML_3 portion of the molecule. This latter distortion may be measured quantitatively by considering the relative orientations of the plane of the five-membered ring and that defined by points equidistant from the metal atom along the Ru–C(1), Ru–N(2), and Ru–P bond vectors. The normals to these planes, which would be parallel in ideal $C_5H_5ML_3$ geometry, form an angle of 13.9°. The corresponding angles in the related iron complexes are 13° in $(C_5H_5C_2CO_2CH_3)_3Fe(CO)_2$[18] and 8.6° in $C_8H_8COFe(CO)_2$.[19]

Table IV. Intramolecular Distances (Å)

Ru–C1	2.013 (6)	C11–C12	1.371 (11)
Ru–N2	2.020 (5)	C12–C7	1.370 (10)
Ru–P	2.284 (2)	C2–F1	1.352 (7)
Ru–C13	2.195 (6)	C3–F2	1.347 (7)
Ru–C14	2.216 (7)	C4–F3	1.362 (7)
Ru–C15	2.238 (7)	C5–F4	1.340 (7)
Ru–C16	2.262 (6)	C8–F5	1.334 (8)
Ru–C17	2.183 (6)	C9–F6	1.343 (10)
N1–N2	1.310 (7)	C10–F7	1.337 (9)
N1–C6	1.365 (8)	C11–F8	1.352 (9)
C1–C2	1.382 (8)	C12–F9	1.334 (9)
C1–C6	1.406 (8)	C13–C14	1.404 (9)
C2–C3	1.353 (9)	C14–C15	1.401 (10)
C3–C4	1.362 (9)	C15–C16	1.407 (10)
C4–C5	1.342 (9)	C16–C17	1.426 (9)
C5–C6	1.388 (8)	C17–C13	1.409 (9)
N2–C7	1.431 (8)	C17–C19	1.474 (7)
C7–C8	1.366 (10)	P–C18	1.804 (4)
C8–C9	1.380 (10)	P–C24	1.826 (4)
C9–C10	1.346 (13)	P–C30	1.812 (4)
C10–C11	1.336 (12)		
		Nonbonded Contacts[a]	
N1· · ·F4	2.746 (7)	N2· · ·F9	2.804 (7)
N1· · ·F5	2.833 (7)	F1· · ·H13	2.483
N2· · ·F5	2.783 (7)	F9· · ·H15	2.365

[a] This tabulation includes N· · ·F intramolecular contacts <2.9 Å and F· · ·H contacts <2.7 Å.

Table V. Bond Angles (deg)

P-Ru–C1	92.4 (2)	C1–C6–N1	117.5 (5)
N2–Ru–C1	75.6 (2)	N2–C7–C8	121.7 (6)
P-Ru–N2	97.8 (2)	N2–C7–C12	121.6 (6)
Ru–P–C18	105.9 (2)	C8–C7–C12	116.6 (6)
Ru–P–C24	119.8 (1)	C7–C8–C9	121.9 (8)
Ru–P–C30	116.2 (1)	C7–C8–F5	119.8 (6)
C18–P–C24	101.0 (2)	C9–C8–F5	118.2 (8)
C18–P–C30	107.9 (2)	C8–C9–C10	119.6 (8)
C24–P–C30	104.6 (2)	C8–C9–F6	118.7 (9)
N2–N1–C6	110.4 (5)	C10–C9–F6	121.6 (8)
Ru–N2–N1	122.0 (4)	C9–C10–C11	119.6 (8)
Ru–N2–C7	127.7 (4)	C9–C10–F7	119.2 (10)
N1–N2–C7	109.8 (5)	C11–C10–F7	121.1 (10)
Ru–C1–C2	131.9 (4)	C10–C11–C12	121.1 (8)
Ru–C1–C6	114.3 (4)	C10–C11–F8	120.1 (8)
C2–C1–C6	113.8 (5)	C12–C11–F8	118.7 (9)
C1–C2–C3	123.3 (6)	C11–C12–C7	121.0 (8)
C1–C2–F1	120.2 (6)	C11–C12–F9	118.1 (8)
C3–C2–F1	116.6 (6)	C7–C12–F9	120.8 (6)
C2–C3–C4	120.4 (6)	C14–C13–C17	107.8 (6)
C2–C3–F2	120.5 (6)	C13–C14–C15	107.8 (6)
C4–C3–F2	119.1 (6)	C14–C15–C16	109.6 (6)
C3–C4–C5	120.6 (6)	C15–C16–C17	106.1 (6)
C3–C4–F3	118.4 (6)	C16–C17–C13	108.6 (6)
C5–C4–F3	120.9 (6)	C13–C17–C19	124.7 (5)
C4–C5–C6	118.4 (6)	C16–C17–C19	126.6 (6)
C4–C5–F4	120.4 (6)	P–C18–C19	114.7 (3)
C6–C5–F4	121.2 (6)	P–C18–C23	125.1 (3)
C5–C6–C1	123.4 (6)	C17–C19–C18	119.4 (4)
C5–C6–N1	119.1 (5)	C17–C19–C20	120.6 (4)

The fluorinated azobenzene ligand is bound in a chelating fashion similar to that observed for unsubstituted azobenzene in two rhodium complexes[20,21] and in a palladium dimer[22] and for azotoluene in a cyclopentadienylnickel complex.[23] The free C_6F_5 group is twisted by an angle of 64.6° from the plane of the five-membered chelate ring. The magnitude of this twist is greater than the range of values of 14–54° previously observed for metalated azobenzene and azotoluene ligands.

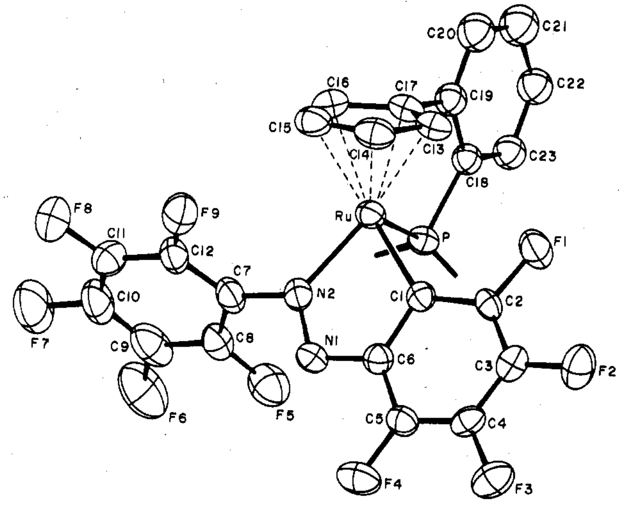

Figure 1. View of the molecular structure of $\overline{\text{RuC}_6\text{F}_4\text{N}}\text{=NC}_6\text{F}_5$-($\text{Ph}_2\text{PC}_6\text{H}_4$-$\eta$-$\text{C}_5\text{H}_4$). Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms and the two free phenyl rings have been omitted for clarity.

This effect is undoubtedly a consequence of the greater steric crowding of the fluorinated ligand, as reflected in the short F···N and F···H contacts listed in Table III. The metal-bound C_6F_4 ring is nearly coplanar (dihedral angle 2.4°) with the chelate ring. The N–N distance of 1.310 (7) Å may be compared with the value 1.24 (3) Å observed in free *trans*-azobenzene[24] and is toward the long end of the range of N–N distances of 1.23–1.34 Å found in complexes containing metalated azobenzene ligands.[25] The two N–C distances (1.365 (8) and 1.431 (8) Å) differ significantly, with the longer distance being to the free C_6F_5 ring. A similar pattern has been observed in some related complexes[20-23] and is consistent with the lesser degree of conjugation expected between the twisted phenyl group and the chelate ring.

The Ru–C distance of 2.013 (6) Å is short in comparison to observed Ru(II)–C(sp^2) distances of 2.160 (10) Å in a σ-naphthylruthenium complex,[26] 2.128 (4) Å in a cationic ruthenium(II)–dimethylimidazolium complex,[27] and 2.10 (1) Å in a binuclear ruthenium complex derived from cyclooctatetraene.[28] Multiple-bond character has been ascribed to a ruthenium–carbene bond of length 2.045 Å.[29] Some evidence exists for shortening of metal–carbon bonds to perfluoroaryl ligands relative to their "normal" values[30] and the above comparisons could be cited in support of such shortening in the present case. However, one Ru(II)–C(sp^2) distance as short as 1.96 (1) Å[31] has been reported and metalated azobenzene complexes of Rh[20,21] and Pd[22] have metal–carbon distances shorter than that observed in the present case. Hence it is not possible to ascribe with confidence any significant shortening to the Ru–C distance. A similar situation exists for the Ru–N distance of 2.020 (5) Å. Comparable distances between a low-valent ruthenium atom and an sp^2 nitrogen include 2.080 (7) Å (mean of four values) in an oxalate-bridged bis(tetrapyridineruthenium(II)) complex,[32] 2.107 (15) Å (mean of three values) in a tetrakis(1-pyrazolyl)boratoruthenium(II) complex,[33] and 2.086 (5) Å in a square-planar ruthenium(II)–phenyldiazene complex.[34] However, metal–nitrogen distances in second transition series metal complexes containing metalated azobenzene ligands[20-22] tend to be comparable in magnitude to the Ru–N distance we observe.

Table VII. Least-Squares Planes

Plane 1: C1, C2, C3, C4, C5, C6
Eq of Plane:[a] $0.3903X + 0.3339Y - 0.8580Z = -4.1564$

Distances to Plane (Å)

C1	0.015	C5	−0.007
C2	−0.004	C6	−0.010
C3	−0.012	N1	−0.054
C4	0.019	N2	0.005

Plane 2: C7, C8, C9, C10, C11, C12
Eq of Plane: $-0.0842X + 0.9905Y - 0.1084Z = 2.1335$

Distances to Plane (Å)

C7	−0.016	C10	−0.018
C8	0.005	C11	0.007
C9	0.012	C12	0.010

Plane 3: C13, C14, C15, C16, C17
Eq of Plane: $0.5094X - 0.5909Y - 0.6255Z = -2.5846$

Distances to Plane (Å)

C13	0.010	C16	0.014
C14	−0.002	C17	−0.015
C15	−0.008	Ru	−1.866

Plane 4: Ru, P, C18, C19, C17[b]
Eq of Plane: $-0.8470X - 0.3426Y - 0.4065Z = 1.7590$

Distances to Plane (Å)

Ru	−0.052	C19	0.007
P	0.067	C17	0.043
C18	−0.064		

Plane 5: Ru, N1, N2, C6, C1
Eq of Plane: $0.3711X + 0.3706Y - 0.8514Z = -3.9527$

Distances to Planes (Å)

Ru	0.005	C6	0.019
N1	−0.012	C1	−0.014
N2	0.002		

Angles between Normals to Planes

Planes	Angle, deg	Planes	Angle, deg
1-2	67.0	3-4	88.6
1-5	2.4	4-5	95.5
2-5	64.6		

[a] Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal system (A, B, C) oriented with respect to the crystallographic axes such that A is parallel to a, B is parallel to $c^* \times a$, and C is parallel to $A \times B$. [b] Although this grouping of atoms clearly is not strictly coplanar, it is included for the purpose of stereochemical comparison with related compounds.

The carbon atoms of the substituted cyclopentadienyl ring are coplanar, and all five C–C distances are equal within experimental error. There is, however, some variation in Ru–C(cyclopentadienyl) distances, which range from 2.183 (6) to 2.262 (6) Å. The C_5H_4 ring is nearly perpendicular (dihedral angle 90.9°) to the phenyl ring to which it is bound. These two rings are linked by a C–C bond of length 1.474 (7) Å, close to the expected value for a single bond between two sp^2 carbon atoms. Other portions of the structure display no unusual features.

By documenting the metalated structure of this ruthenium complex, our structure analysis has confirmed the first example of a metalated complex prepared via abstraction of an atom other than hydrogen. Subsequent work has yielded at least one other instance of metalation by fluorine abstraction, though elimination of a hydrogen atom, where possible, has been shown to take precedence over this pathway.[8] The fact that metalation of perfluorinated azobenzenes occurs lends support to the view[6,7] that the metalation reaction can, under appropriate circumstances, occur via nucleophilic attack on a substituted aromatic ring. The coupling of the η-cyclopentadienyl ring to the triphenylphosphine ligand is unusual. The closest parallel occurs in an iron–triphenyl phosphite complex which contains a similar phenyl–cyclopentadienyl linkage.[35] Although the α-carbon atoms of metal-bound triphenylphosphine groups are known to undergo metalation and exchange[36] reactions, there appears to be no direct precedent for the coupling of a triphenylphosphine ligand to an η-cyclopentadienyl group. The mechanism of this coupling and its role in the overall reaction sequence are not clear.

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Registry No. $\overline{\mathrm{RuC_6F_4N{=}N}}\mathrm{C_6F_5(Ph_2PC_6H_4\text{-}\eta\text{-}C_5H_4)}$, 59569-15-2.

Supplementary Material Available: A listing of structure factor amplitudes and Table VI, giving principal amplitudes of thermal motion (23 pages). Ordering information is given on any current masthead page.

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Unusual Hydrogen Bonds. A Neutron Diffraction Study of the Hydrogen Dinitrate Ion, $(\mathrm{O_2NO{\cdot}H{\cdot}ONO_2})^-$, in Cesium Hydrogen Dinitrate[1]

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The crystal structure of cesium hydrogen dinitrate, $\mathrm{Cs^+(O_2NO{\cdot}H{\cdot}ONO_2)^-}$, has been determined from three-dimensional single-crystal neutron-diffraction data. The crystals are orthorhombic, space group *Fddd*, with eight formula units in the unit cell of dimensions a = 12.527 (6) Å, b = 7.344 (3) Å, and c = 12.983 (6) Å. A full-matrix least-squares refinement based on F_o^2 gave a final R value of 0.050 for 391 independent reflections (derived from 1059 measured data) with intensities greater than $\sigma(F_o^2)$. The hydrogen dinitrate ion consists of two nitrate groups related by a very short [O···O = 2.468 (8) Å] and symmetric hydrogen bond. In the crystal the hydrogen dinitrate ions are shown to be orientationally disordered. This orientational disorder was not recognized in the previous x-ray studies and resulted in an apparent pseudo-tetrahedral coordination of the hydrogen atom and (O···O) $\simeq$ 2.8–3.1 Å. Analysis of the thermal motion of the bridging hydrogen atom is consistent with a symmetric single-minimum potential well in the short hydrogen bond.

Introduction

As has been discussed in a previous x-ray structure publication,[2] the hydrogen dinitrate ion, $(\mathrm{O_2NO{\cdot}H{\cdot}ONO_2})^-$, apparently occurs in the crystalline state in two distinctly different configurations.[3,4] The first configuration, observed only in the tetraphenylarsonium (TPA) salt,[3] consists of two coplanar unidendate nitrate groups linked across a center of symmetry by a very short hydrogen bond (O···O $\simeq$ 2.45 Å) and is very similar to that of some acid salts of organic monobasic acids referred to as type A using Speakman's classification.[5] The second and most frequently occurring configuration involves four oxygen atoms of two nitrate groups which surround a bridging hydrogen atom forming a distorted tetrahedron. The latter, rather unusual, configuration has been observed with cations of various sizes such as $[\mathrm{Rh(py)_4Cl_2}]^+$ [4] and $\mathrm{(CH_3)_4N^+}$.[6] In all cases at least one twofold symmetry axis relates the two nitrate groups. Although the $\mathrm{H(NO_3)_2^-}$ infrared spectrum has been previously interpreted[7] in terms of a short (at most 2.5 Å O···O separation) and quasi-symmetrical hydrogen bond, the O···O distances observed in the x-ray studies appear to be much longer and range between 2.85 and 3.15 Å. The stability of the tetrahedral configuration has been shown recently to have a sound theoretical basis.[8] This neutron diffraction study of $\mathrm{CsH(NO_3)_2}$ was first undertaken to obtain precise information on the location and dynamics of the bridging hydrogen atom in a simple system with a tetrahedrally coordinated hydrogen. While the results (vide infra) were somewhat unexpected they completely reconcile