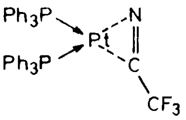
Cyclopentadienyl-ruthenium and -osmium Chemistry. Part 14.[1] The Reaction Between Chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium and Trifluoroacetonitrile: Crystal Structure of $[\mathrm{RuNH{=}C(CF_3)N{=}C(CF_3)NH\{P(OMe)_3\}(\eta\text{-}C_5H_5)}]$ †

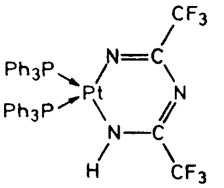
By **Valerie Robinson, Graham E. Taylor,** and **Peter Woodward,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS
Michael I. Bruce * and **Robert C. Wallis,** Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001

The reaction between $\mathrm{CF_3CN}$ and $[\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_5)}]$ affords $[\mathrm{RuNH{=}C(CF_3)N{=}C(CF_3)NH(PPh_3)(\eta\text{-}C_5H_5)}]$; exchange with $\mathrm{P(OMe)_3}$ gives the corresponding trimethyl phosphite complex, whose structure has been determined by *X*-ray diffraction methods. The complex contains a planar metallocycle in which the ruthenium atom is bonded on both sides to NH, then through $\mathrm{C(CF_3)}$ to a lone nitrogen atom. The co-ordination around the metal atom is octahedral (with $\mathrm{C_5H_5}$ occupying three sites) and the orthogonality is preserved despite the requirements of the ring geometry. The bonds within the ring are delocalised to give effective mirror symmetry across the Ru . . . N vector, with mean bond lengths: Ru–NH, 2.078(5); HN–$\mathrm{C(CF_3)}$, 1.287(8); $\mathrm{(CF_3)C{-}N}$, 1.339(9); and C–$\mathrm{CF_3}$, 1.514(11) Å. The angles at N(H) and $\mathrm{C(CF_3)}$ adjust to accommodate these rather varied bond lengths, but the angle at the unique N atom remains 120°. Within the cyclopentadienyl ring the Ru–C distances vary between 2.15 and 2.27 Å, the longer ones being *trans* to the Ru–P bond.

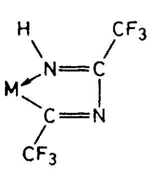
REACTIONS between trifluoroacetonitrile, $\mathrm{CF_3CN}$, and transition-metal complexes have resulted in the formation of complexes of a variety of structural types. Treatment of $[\mathrm{Pt}(\textit{trans}\text{-stilbene})\mathrm{(PPh_3)_2}]$ with excess of $\mathrm{CF_3CN}$ afforded $[\mathrm{Pt(\eta^2\text{-}N{\equiv}CCF_3)(PPh_3)_2}]$ (1); a similar reaction with $[\mathrm{Pt(PPh_3)_4}]$ gave in addition the complex $[\mathrm{PtN{=}C(CF_3)N{=}C(CF_3)NH(PPh_3)_2}]$, (2).[2] An iron complex, originally obtained from the reaction with $[\mathrm{FeMe(CO)_2(\eta\text{-}C_5H_5)}]$,[3] has been crystallographically characterised as $[\mathrm{FeNH{=}C(CF_3)N{=}C(CF_3)(CO)(\eta\text{-}C_5H_5)}]$, (3).[4] The same paper also describes a similar iridium complex $[\mathrm{IrNH{=}C(CF_3)N{=}C(CF_3)(CO)(PPh_3)_2}]$, (4), obtained from $[\mathrm{IrH(CO)_2(PPh_3)_2}]$, $[\mathrm{IrH(CO)(PPh_3)_3}]$, or $[\mathrm{Ir(\eta^3\text{-}CH_2CHCHMe)(CO)(PPh_3)_2}]$ and $\mathrm{CF_3CN}$; a minor product formed in variable yields from the reaction between $\mathrm{CF_3CN}$ and $[\mathrm{Ir(CO)(PPh_3)_2(\eta^3\text{-}C_3H_5)}]$ was identified as $[\mathrm{IrNH{=}C(CF_3)N{=}C(CF_3)NH(CO)(PPh_3)_2}]$, (5).



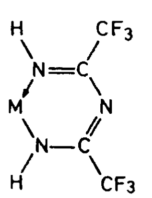
(1)



(2)



(3) M = $\mathrm{Fe(CO)(\eta\text{-}C_5H_5)}$
(4) M = $\mathrm{Ir(CO)(PPh_3)_2}$



(5) M = $\mathrm{Ir(CO)(PPh_3)_2}$
(6) M = $\mathrm{Ru(PPh_3)(\eta\text{-}C_5H_5)}$
(7) M = $\mathrm{Ru\{P(OMe)_3\}(\eta\text{-}C_5H_5)}$

RESULTS AND DISCUSSION

We have previously described the reactions of $[\mathrm{RuCl(PPh_3)(\eta\text{-}C_5H_5)}]$ with a series of nitriles, RCN, in methanol in the presence of ammonium hexafluorophosphate, which result in the formation of the cationic complexes $[\mathrm{Ru(NCR)(PPh_3)_2(\eta\text{-}C_5H_5)}][\mathrm{PF_6}]$ (*e.g.* R = Me, $\mathrm{CH_2Cl}$, Ph, $\mathrm{C_6F_5}$, *etc.*).[5] A similar reaction with trifluoroacetonitrile gave only a small amount of a hexafluorophosphate salt, probably $[\mathrm{Ru(NCCF_3)(PPh_3)_2(\eta\text{-}C_5H_5)}][\mathrm{PF_6}]$, the major product being a red-orange neutral complex (6). The latter could be obtained as the only product in 79% yield in the absence of $[\mathrm{NH_4}][\mathrm{PF_6}]$; however, when tetrahydrofuran was used as solvent in place of methanol, no reaction occurred.

Complex (6) has elemental analyses corresponding with the formulation $[\mathrm{Ru\{N(CF_3CNH)_2\}(PPh_3)(\eta\text{-}C_5H_5)}]$, and this is confirmed by the presence of a parent ion *m/e* 635 in the mass spectrum of (6). In the i.r. spectrum, weak ν(NH) bands are found at 3 387 and 3 371 $\mathrm{cm^{-1}}$; and other strong bands may be assigned to ν(CN) and ν(CF) modes. The relative intensities of the $\mathrm{PPh_3}$ and $\mathrm{C_5H_5}$ resonances in the ^{1}H n.m.r. spectrum are 3 : 1; in the ^{19}F n.m.r. spectrum, a singlet at 87.4 p.p.m. (downfield from $\mathrm{C_6F_6}$) shows the equivalence of the two $\mathrm{CF_3}$ groups. In the ^{13}C n.m.r. spectrum, the usual signals at δ 76.6, and between δ 128.5 and 136.2, confirmed the presence of $\mathrm{C_5H_5}$ and $\mathrm{PPh_3}$ ligands, respectively. Two other signals, at δ 117.8 and 154.1, both with quartet fine

---

† [1,3-Bis(trifluoromethyl)-2,4-diazabutadienylamido-*N,N''*]-(η-cyclopentadienyl)(trimethyl phosphite)ruthenium.

structure, can be assigned to the CF_3 and C=N carbons, respectively.

On heating (6) with trimethyl phosphite in decalin for a short period, phosphine–phosphite exchange occurs, and red crystals of $[Ru\{N(CF_3CNH)_2\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (7) may be isolated. The spectroscopic properties of this complex resemble those of (6), except for the anticipated changes resulting from the presence of the $P(OMe)_3$ ligand.

A possible formulation for the fluorine-containing ligand is the chelating azadi-imino-system found in (5), and this has been confirmed by a single-crystal *X*-ray study of complex (7). The overall configuration of the molecule, with the crystallographic numbering sequence, is shown in Figure 1, and the numerical data from the *X*-ray analysis are in Tables 1 and 2. Interest centres on the Ru–N–C–N–C–N ring system. All the atoms of the metallocycle, together with the H atoms on N(1) and N(3) and the carbon atoms of the trifluoromethyl groups, C(3) and C(4), are coplanar within 0.06 Å. Moreover, the CF_3 groups are themselves arranged symmetrically with respect to the plane of the ring, as Figure 2 clearly shows. Atoms F(1) and F(4) lie in the plane, while F(3) mirrors F(2) and F(6) mirrors F(5). The two hydrogen atoms are uniquely associated with N(1) and N(3). As might be expected, there is extensive bond delocalisation within the ring, although the Ru · · · N(2) vector divides the ring into two equivalent halves. The bond angles within the ring are such as to maintain octahedral bonding for Ru (84°) and trigonal planar bonding for N(2) (120°). Thus we find Ru–N–C angles *ca.* 128° and N–C–N angles of 131°. The bond lengths show interesting variations of the kind found earlier [4] in our study of $[FeNHC(CF_3)NHC(CF_3)(CO)(\eta\text{-}C_5H_5)]$, in that the two nitrogen atoms bonded to the metal atom form unusually short links to the carbon atom of the adjacent $C(CF_3)$ group. The mean value for all four bonds of the type N(1)–C(1) (there are two crystallographically different molecules in the asymmetric unit) is 1.28_8 Å (*cf.* 1.27_2 in the iron compound) as compared with 1.34_0 for the four bonds of type C(1)–N(2). This shortening of bonds in metallocycles between an electronegative element attached to the metal and an adjacent carbon atom surrounded by electronegative ligands has been discussed earlier.[6] The Ru–N bonds are all equivalent within experimental error at 2.07_8 Å. The C–CF_3 bonds have a mean value of 1.51_4 Å, slightly shorter than is sometimes found in delocalised systems,[7] but in fact equal to the sum of the covalent radii [8] for Csp^3–Csp^2: $(0.77 + 0.74) = 1.51$ Å. The mean C–F bond length is 1.33_0 Å, very close to the mean found in many fluorocarbons.[9] It should be noted, however, that the thermal parameters for the fluorine atoms are (as often) very high, and that any correction of the bond length for libration effects would tend to enlarge this value. The F–C–F angles are all rather less than the ideal tetrahedral value, giving increased *p* character to the C–F bonds and increased *s* character to the C–CF_3 links.

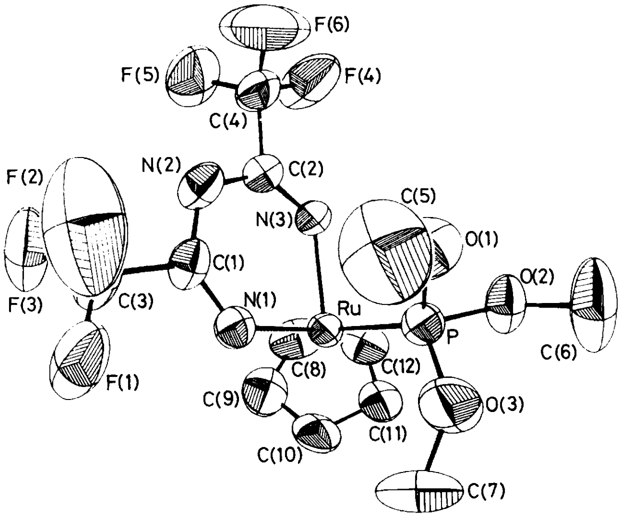


FIGURE 1 Molecular structure of (7), $[RuNH=C(CF_3)N=C(CF_3)NH\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$, showing the crystallographic atom numbering

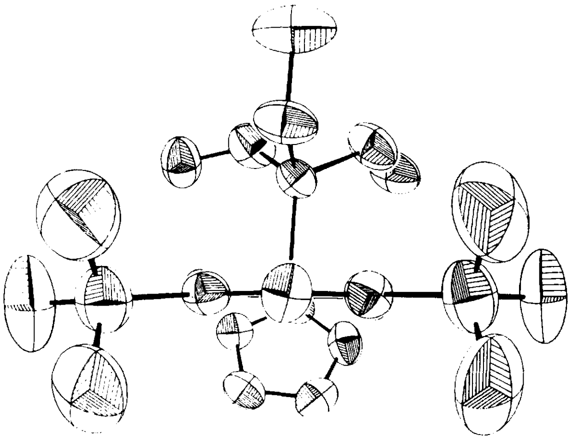


FIGURE 2 The molecule (7) seen edgewise in relation to the metallocycle

For the $Ru(\eta\text{-}C_5H_5)$ moiety the dimensions are as found in other structures, but it may be noted that differences among the individual Ru–C_5 bond lengths appear to be significant, and that the longest of these, Ru–C(8) and Ru–C(9), lie *trans* to the phosphite ligand.

The phosphite geometry calls for no comment except that the Ru–P distance of 2.22_4 Å is similar to that found in $[Ru\{C_3(CN)_5\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)]$ (2.23_9 Å).[10]

The earlier complexes containing ligands derived from two molecules of CF_3CN are of three types. In the first, exemplified by complexes (3) and (4), a head-to-tail dimerisation of CF_3CN, followed by hydrogen shift from metal to nitrogen, affords the five-membered metallocyclic system $M[C(CF_3)=NC(CF_3)=NH]$ (M = Fe or Ir). The sole example of the second type is the six-membered $Pt[N=C(CF_3)N=C(CF_3)NH]$ system found in complex (2).

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Molecule 1			
Ru	0.191 68(4)	0.642 34(3)	0.371 39(3)
N(1)	0.368 2(4)	0.552 4(3)	0.362 8(4)
C(1)	0.495 7(5)	0.560 6(4)	0.346 8(4)
N(2)	0.552 9(4)	0.626 8(3)	0.329 5(4)
C(2)	0.470 7(5)	0.698 8(3)	0.328 6(4)
N(3)	0.335 4(4)	0.717 0(3)	0.337 7(3)
H(1)	0.369(6)	0.513(4)	0.369(5)
H(3)	0.304(5)	0.754(3)	0.335(4)
C(3)	0.607 2(6)	0.486 2(4)	0.346 7(6)
F(1)	0.556 2(4)	0.419 1(3)	0.361 6(5)
F(2)	0.678 5(5)	0.446 2(3)	0.254 8(4)
F(3)	0.701 4(4)	0.518 7(3)	0.427 9(5)
C(4)	0.557 0(6)	0.768 5(4)	0.317 6(5)
F(4)	0.481 5(4)	0.843 8(3)	0.321 7(4)
F(5)	0.651 0(4)	0.801 2(3)	0.399 1(4)
F(6)	0.626 9(6)	0.734 5(3)	0.225 5(4)
P	0.162 41(15)	0.556 40(10)	0.189 27(12)
O(1)	0.297 6(4)	0.538 5(3)	0.118 0(3)
C(5)	0.302 8(8)	0.481 5(6)	−0.003 0(6)
O(2)	0.036 4(5)	0.584 2(3)	0.125 9(4)
C(6)	0.005 2(8)	0.680 5(5)	0.142 7(6)
O(3)	0.131 5(5)	0.448 6(3)	0.147 8(4)
C(7)	0.010 6(8)	0.424 3(5)	0.183 2(7)
C(8) [a]	0.109 1(5)	0.763 7(2)	0.529 7(4)
C(9)	0.139 3(5)	0.683 8(2)	0.550 6(4)
C(10)	0.055 4(5)	0.613 1(2)	0.476 5(4)
C(11)	−0.026 6(5)	0.649 3(2)	0.409 8(4)
C(12)	0.006 6(5)	0.742 4(2)	0.442 7(4)
H(8) [b]	0.151	0.822	0.568
H(9)	0.205	0.678	0.605
H(10)	0.054	0.552	0.472
H(11)	−0.093	0.617	0.353
H(12)	−0.033	0.784	0.412
(*b*) Molecule 2 (atom numbers as for molecule 1 with primes)			
Ru′	0.439 39(5)	0.062 58(3)	0.228 00(3)
N′(1)	0.281 0(5)	0.041 9(3)	0.312 9(4)
C′(1)	0.212 2(6)	−0.031 5(4)	0.281 1(5)
N′(2)	0.216 9(5)	−0.109 5(3)	0.188 3(4)
C′(2)	0.311 1(6)	−0.122 3(4)	0.108 7(5)
N′(3)	0.398 9(5)	−0.067 7(3)	0.104 9(3)
H′(1)	0.270(5)	0.072(3)	0.371(4)
H′(3)	0.441(5)	−0.083(3)	0.058(4)
C′(3)	0.109 6(7)	−0.033 8(4)	0.362 8(6)
F′(1)	0.100 5(7)	0.040 7(3)	0.454 0(5)
F′(2)	−0.016 2(5)	−0.045 0(6)	0.323 5(6)
F′(3)	0.142 0(5)	−0.101 2(3)	0.392 2(4)
C′(4)	0.308 6(9)	−0.220 8(4)	0.013 8(5)
F′(4)	0.395 3(7)	−0.236 3(3)	−0.065 2(4)
F′(5)	0.332 7(6)	−0.284 8(3)	0.046 8(4)
F′(6)	0.181 5(7)	−0.234 2(4)	−0.031 6(5)
P′	0.282 57(16)	0.131 89(10)	0.153 13(12)
O′(1)	0.145 6(5)	0.079 4(4)	0.092 8(5)
C′(5)	0.013 7(9)	0.088 9(9)	0.144 5(10)
O′(2)	0.340 9(5)	0.146 8(3)	0.053 3(4)
C′(6)	0.252 9(11)	0.200 6(7)	0.001 9(7)
O′(3)	0.210 5(7)	0.232 4(3)	0.226 4(4)
C′(7)	0.245 3(11)	0.293 1(5)	0.334 9(7)
C′(8) [a]	0.663 4(5)	0.019 7(4)	0.256 2(3)
C′(9)	0.602 8(5)	0.077 6(4)	0.361 5(3)
C′(10)	0.558 9(5)	0.165 7(4)	0.363 0(3)
C′(11)	0.592 3(5)	0.162 2(4)	0.258 6(3)
C′(12)	0.656 9(5)	0.072 0(4)	0.192 6(3)
H′(8) [b]	0.702	−0.044	0.232
H′(9)	0.593	0.060	0.421
H′(10)	0.514	0.218	0.424
H′(11)	0.574	0.212	0.237
H′(12)	0.690	0.050	0.118

[a] The C atoms of the cyclopentadienyl ligand were constrained to regular pentagonal geometry with C–C = 1.420 Å during refinement. [b] H atoms of the cyclopentadienyl ligand are in calculated positions (C–H = 0.960 Å, U_H = 0.097 Å^2).

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances			
(*i*) Metallocycles			
Ru–N(1)	2.078(4)	Ru′–N′(1)	2.070(5)
N(1)–C(1)	1.276(7)	N′(1)–C′(1)	1.294(8)
C(1)–N(2)	1.345(9)	C′(1)–N′(2)	1.320(6)
N(2)–C(2)	1.331(7)	N′(2)–C′(2)	1.362(8)
C(2)–N(3)	1.295(6)	C′(2)–N′(3)	1.286(8)
N(3)–Ru	2.089(5)	N′(3)–Ru′	2.075(4)
N(1)–H(1)	0.694(69)	N′(1)–H′(1)	0.742(43)
N(2)–H(2)	0.675(57)	N′(2)–H′(2)	0.722(47)
C(1)–C(3)	1.514(8)	C′(1)–C′(3)	1.519(11)
C(3)–F(1)	1.314(10)	C′(3)–F′(1)	1.280(7)
C(3)–F(2)	1.303(8)	C′(3)–F′(2)	1.281(9)
C(3)–F(3)	1.322(8)	C′(3)–F′(3)	1.302(10)
C(2)–C(4)	1.510(9)	C′(2)–C′(4)	1.535(7)
C(4)–F(4)	1.319(8)	C′(4)–F′(4)	1.297(10)
C(4)–F(5)	1.324(7)	C′(4)–F′(5)	1.275(10)
C(4)–F(6)	1.299(8)	C′(4)–F′(6)	1.320(10)
(*ii*) Phosphite ligand			
Ru–P	2.229(1)	Ru′–P′	2.219(2)
P–O(1)	1.573(5)	P′–O′(1)	1.605(5)
P–O(2)	1.570(5)	P′–O′(2)	1.587(6)
P–O(3)	1.618(5)	P′–O′(3)	1.582(5)
O(1)–C(5)	1.470(5)	O′(1)–C′(5)	1.432(12)
O(2)–C(6)	1.457(9)	O′(2)–C′(6)	1.489(13)
O(3)–C(7)	1.419(10)	O′(3)–C′(7)	1.392(9)
(*iii*) Cyclopentadienyl rings:	all C–C bonds fixed at 1.420 Å all C–H bonds fixed at 0.960 Å		
C(8)–Ru	2.273(3)	C′(8)–Ru′	2.242(5)
C(9)–Ru	2.255(5)	C′(9)–Ru′	2.248(4)
C(10)–Ru	2.181(5)	C′(10)–Ru′	2.197(4)
C(11)–Ru	2.153(4)	C′(11)–Ru′	2.159(5)
C(12)–Ru	2.210(4)	C′(12)–Ru′	2.187(5)
(*b*) Angles			
N(1)–Ru–N(3)	83.6(2)	N′(1)–Ru′–N′(3)	84.4(2)
N(1)–Ru–P	87.1(1)	N′(1)–Ru′–P′	90.3(2)
N(3)–Ru–P	89.8(1)	N′(3)–Ru′–P′	91.2(1)
(*i*) Metallocyclic rings			
Ru–N(1)–C(1)	128.1(4)	Ru′–N′(1)–C′(1)	127.1(4)
N(1)–C(1)–N(2)	130.7(5)	N′(1)–C′(1)–N′(2)	131.4(6)
C(1)–N(2)–C(2)	119.5(5)	C′(1)–N′(2)–C′(2)	119.2(5)
N(2)–C(2)–N(3)	130.6(6)	N′(2)–C′(2)–N′(3)	130.5(4)
C(2)–N(3)–Ru	127.3(4)	C′(2)–N′(3)–Ru′	127.2(3)
Ru–N(1)–H(1)	125.1(47)	Ru′–N′(1)–H′(1)	119.4(43)
Ru–N(2)–H(2)	110.4(47)	Ru′–N′(2)–H′(2)	112.8(37)
C(1)–N(1)–H(1)	105.4(47)	C′(1)–N′(1)–H′(1)	110.7(46)
C(2)–N(2)–H(2)	120.8(47)	C′(2)–N′(2)–H′(2)	118.5(38)
(*ii*) CF_3 Groups			
N(1)–C(1)–C(3)	118.1(6)	N′(1)–C′(1)–C′(3)	117.4(5)
N(2)–C(1)–C(3)	111.1(5)	N′(2)–C′(1)–C′(3)	111.2(5)
C(1)–C(3)–F(1)	113.5(5)	C′(1)–C′(3)–F′(1)	113.5(6)
F(1)–C(3)–F(2)	106.5(5)	F′(1)–C′(3)–F′(2)	105.7(6)
F(1)–C(3)–F(3)	104.1(7)	F′(1)–C′(3)–F′(3)	105.4(7)
F(2)–C(3)–F(3)	105.9(5)	F′(2)–C′(3)–F′(3)	105.3(8)
N(3)–C(2)–C(4)	118.4(5)	N′(3)–C′(2)–C′(4)	119.1(5)
N(2)–C(2)–C(4)	110.9(5)	N′(2)–C′(2)–C′(4)	110.4(6)
C(2)–C(4)–F(4)	113.6(5)	C′(2)–C′(4)–F′(4)	112.9(6)
F(4)–C(4)–F(5)	104.2(5)	F′(4)–C′(4)–F′(5)	108.9(6)
F(4)–C(4)–F(6)	106.4(7)	F′(4)–C′(4)–F′(6)	107.3(6)
F(5)–C(4)–F(6)	106.1(5)	F′(5)–C′(4)–F′(6)	103.7(7)
(*iii*) Phosphite ligands			
Ru–P–O(1)	114.6(2)	Ru′–P′–O′(1)	118.4(3)
Ru–P–O(2)	119.4(2)	Ru′–P′–O′(2)	114.2(2)
Ru–P–O(3)	117.9(2)	Ru′–P′–O′(3)	120.6(2)
O(1)–P–O(2)	106.7(3)	O′(1)–P′–O′(2)	99.2(3)
O(2)–P–O(3)	97.4(3)	O′(2)–P′–O′(3)	101.1(3)
O(3)–P–O(1)	97.4(2)	O′(3)–P′–O′(1)	99.8(3)
P–O(1)–C(5)	123.7(4)	P′–O′(1)–C′(5)	125.9(5)
P–O(2)–C(6)	121.0(4)	P′–O′(2)–C′(6)	120.6(5)
P–O(3)–C(7)	121.2(4)	P′–O′(3)–C′(7)	127.8(6)

Our complexes (6) and (7) join the iridium derivative (5) as examples of complexes containing the three-electron donor di-imino-ligand, also forming six-membered chelate systems.

We have been able to adduce little evidence concerning the source of the extra nitrogen atom. Kemmitt and co-workers [2] have suggested that the third nitrogen atom in the chelate ligand of (2) arises by an *in situ* degradation of CF_3CN by traces of water. A similar explanation was advanced, with reservations, to account for the formation of (5).[4] In our case, it is significant that the chelate complex is formed in high yield in methanol (wet or dry), but does not form to any appreciable extent when dry tetrahydrofuran is used as the reaction medium.

EXPERIMENTAL

General experimental conditions are similar to those described in earlier papers of this series.

Preparation of $[\mathrm{RuNHC(CF_3){=}NC(CF_3){=}NH(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]$, (6).—Trifluoroacetonitrile (2.0 g, 2.1 mmol) was condensed into a Carius tube containing $[\mathrm{RuCl(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]$ (500 mg, 0.69 mmol) and methanol (40 cm^3). After sealing, the tube and contents were heated (100 °C for 1 day) until all of the chloro-complex had reacted. Evaporation of solvent and chromatography of the residue (alumina) gave an orange-red fraction eluted with diethyl ether. Crystallisation (light petroleum) afforded red *crystals* of $[\mathrm{RuNHC(CF_3){=}NC(CF_3){=}NH(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]$, (6) (340 mg, 79%), m.p. 146—147 °C [Found: C, 51.4; H, 3.6; N, 6.6%; *M* (mass spectrometry), 635. $\mathrm{C_{27}H_{22}F_6N_3PRu}$ requires C, 51.4; H, 3.5; N, 6.7%; *M*, 635]. Infrared (Nujol): ν(NH) 3 387m, 3 371m; ν(C=N) 1 585m, 1 550m, 1 520m; ν(CF) 1 260s, 1 175s, 1 155(sh) cm^{-1}. ^{1}H N.m.r.: δ ($CDCl_3$) 4.29, s, 5 H, C_5H_5; 7.39, 7.46, m, 15 H, PPh_3. ^{13}C N.m.r.: δ ($CDCl_3$) 76.6, s, C_5H_5; 117.8, q, *J*(CF) 280 Hz, CF_3; 128.5—136.2, m, PPh_3; 154.1, q, *J*(CF) 33 Hz, =*C*(CF_3). ^{19}F N.m.r.: −87.54 p.p.m. (relative to internal C_6F_6), s, CF_3.

Preparation of $[\mathrm{RuNHC(CF_3){=}NC(CF_3){=}NH\{P(OMe)_3\}}(\eta\text{-}\mathrm{C_5H_5})]$, (7).—A mixture of complex (6) (250 mg, 0.39 mmol) and trimethyl phosphite (250 mg, 2.01 mmol) was heated in refluxing decalin (1 h). Removal of solvent and chromatography (alumina) gave an orange-red band, eluted with light petroleum, which was crystallised to give red *crystals* of pure $[\mathrm{RuNHC(CF_3){=}NC(CF_3){=}NH\{P(OMe)_3\}}(\eta\text{-}\mathrm{C_5H_5})]$, (7), m.p. 105—107 °C [Found: C, 29.3; H, 3.2; N, 8.3%; *M* (mass spectrometry), 497. $\mathrm{C_{12}H_{16}F_6N_3O_3PRu}$ requires C, 29.0; H, 3.3; N, 8.5%; *M*, 497]. Infrared (Nujol): ν(NH) 3 355w, 3 290w; ν(C=N) 1 586m, 1 546m; ν(CF) 1 274s, 1 125s; ν(PO) 1 024s cm^{-1}. ^{1}H N.m.r.: δ ($CDCl_3$) 5.48, d, *J*(HP) 1.2 Hz, 5 H, C_5H_5; 6.47, d, *J*(HP) 11.5 Hz, 9 H, POMe. ^{13}C N.m.r.: δ ($CDCl_3$) 51.1, d, *J*(CP) 4 Hz, PO*Me*; 77.4, d, *J*(CP) 4 Hz, C_5H_5; 117.9, q, *J*(CF) 281 Hz, CF_3; 154.7, q, *J*(CF) 33 Hz, =*C*(CF_3).

Crystal Structure Determination of $[\mathrm{RuNH{=}C(CF_3)N{=}C(CF_3)NH\{P(OMe)_3\}}(\eta\text{-}\mathrm{C_5H_5})]$, (7).—Complex (7) crystallises from light petroleum as red parallelepipeds showing faces (100), (011), and (01$\bar{1}$), with some development of facets (010). The crystal chosen for intensity measurements, 0.16 × 0.40 × 0.25 mm, was mounted on a Nicolet R3/M four-circle diffractometer at room temperature according to methods described earlier.[6] Of the total 8 726 independent intensities recorded to $2\theta = 55°$, 5 598 had $F > 6.0\,\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. Remeasurement of reflections $\bar{1}\ \bar{6}\ 8$ and $3\ \bar{4}\ 7$ every 50 reflections showed no significant crystal decay. No correction for *X*-ray absorption was made [μ(Mo-K_α) = 9.5 cm^{-1}].

*Crystal data.** $\mathrm{C_{12}H_{16}F_6N_3O_3PRu}$, $M = 496.3$, Triclinic, $a = 9.544(2)$, $b = 15.979(3)$, $c = 13.324(2)$ Å, $\alpha = 115.67(3)$, $\beta = 93.16(3)$, $\gamma = 84.31(3)°$, $U = 1\,822.1(9)$ Å^3, $D_m = 1.78$, $Z = 4$, $D_c = 1.79$ g cm^{-3}, $F(000) = 984$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.5 cm^{-1}.

Structure solution and refinement. The structure was solved by heavy-atom methods, first to yield Ru atom locations for two crystallographically different molecules and then, from electron-density difference maps, the locations of all non-hydrogen atoms. The hydrogen atoms of the imino-groups of the metallocycle were located from electron-density maps and were refined with U_H fixed at 0.097 Å^2. The cyclopentadienyl ring was treated as a rigid group † with C–C = 1.420 and C–H = 0.960 Å. The hydrogen atoms of the methyl phosphite groups were omitted. Refinement by blocked-cascade least squares, with anisotropic thermal parameters for all non-hydrogen atoms, led to *R* 0.048 (*R′* 0.047), and a weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0005\,|F_o|^2$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.7 e Å^{-3} except in the immediate neighbourhood of the Ru atoms where peaks *ca.* 1.0 e Å^{-3} occurred. Scattering factors were from ref. 11 for all non-hydrogen atoms and ref. 12 for hydrogen. All computations were carried out on an 'Eclipse' (Data General) Minicomputer with the 'SHELXTL' system of programs.[13] Observed and calculated structure factors and all thermal parameters are listed in Supplementary Publication No. SUP 23003 (36 pp.).‡

We thank the S.R.C. and the Australian Research Grants Committee for support. Part of this work was done while R. C. W. was recipient of a Commonwealth Postgraduate Research Award.

[0/1493 *Received, 29th September*, 1980]

---

* A preliminary investigation of crystals of complex (6) showed, surprisingly, a monoclinic unit cell of approximate dimensions $a = 32.3$, $b = 14.3$, $c = 23.5$ Å, $\beta = 97.7°$, $Z = 16$, space group $P2_1/n$. Because of the large size of the unit cell, and (apparently) the presence of *four* molecules of (6) per asymmetric unit, and also because of the availability of (7), this *X*-ray analysis was abandoned.

† The cyclopentadienyl rings were treated as rigid groups because (*i*) this enables the data-to-variable ratio to be kept as high as possible; (*ii*) any differences among the five C–C bond lengths would be unlikely to appear as significant in an individual atom refinement when the estimated standard deviations on these distances are *ca.* 0.008 Å. Differences among the Ru–C distances would, however, still be expected to appear if real, and this did in fact occur.

‡ For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

REFERENCES

[1] Part 13, M. I. Bruce and R. C. Wallis, *Aust. J. Chem.*, 1981, **34**, 209.

[2] W. J. Bland, R. D. W. Kemmitt, I. W. Nowell, and D. R.

Russell, *Chem. Commun.*, 1968, 1065; W. J. Bland, R. D. W. Kemmitt, and R. D. Moore, *J. Chem. Soc., Dalton Trans.*, 1973, 1292.

[3] R. B. King and K. H. Pannell, *J. Am. Chem. Soc.*, 1968, **90**, 3984.

[4] M. Bottrill, R. Goddard, M. Green, R. P. Hughes, M. K. Lloyd, S. H. Taylor, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1975, 1150.

[5] G. S. Ashby, M. I. Bruce, I. B. Tomkins, and R. C. Wallis, *Aust. J. Chem.*, 1979, **32**, 1003.

[6] A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065, and refs. therein.

[7] 'Molecular Structures and Dimensions,' eds. O. Kennard and D. G. Watson, Interatomic Distances, 1960—1965, vol. A1, Cambridge Crystallographic Data Centre.

[8] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, New York, 1972.

[9] 'Table of Interatomic Distances and Configuration in Molecules and Ions,' Supplement 1956—1959, ed. L. E. Sutton, *Special Publ.*, The Chemical Society, London, 1965, no. 18.

[10] M. I. Bruce, R. C. Wallis, and A. H. White, unpublished work.

[11] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[13] G. M. Sheldrick, SHELXTL programs for use with the Nicolet R3/M *X*-ray system, Cambridge, 1976.