Atomic coordinates are provided in Table II, selected bond distances and angles in Table III, and least-squares planar calculations in Table IV. Additional data are available as supplementary material.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-85-0228.

Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (4 pages); a listing of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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Chelation of a C–F Bond to Iridium in an 8-Fluoroquinoline Complex

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We have previously shown that cationic iridium(I)[1] and -(III)[2] complexes can bind the lone pairs of iodo-, bromo- and chlorocarbons to give complexes. In each case the M–X distance is equal to the sum of the covalent radii and the angle C–X–M is near 102°. This angle is, we believe, consistent with binding to the largely p-type lone pairs on the halogen. Fluorocarbons such as o-C_6H_4BrF did not bind via the C–F bond in analogous systems.[2] We were therefore prompted to use 8-fluoroquinoline, because we had previously found[3] that 8-methylquinoline gives the agostic system $[IrH_2L_2(8\text{-}MeC_9H_6N)]^+$, in a case where the corresponding methane complex is unknown.

Beck has given IR evidence[4] for halocarbon binding to various transition-metal cations; Uson, Cotton, et al. have reported a bromocarbon[5] and fluorocarbon[6] example, and Richards has a fluorocarbon case.[7]

Results and Discussion

Hydrogenation of $[Ir(cod)(PPh_3)_2]SbF_6$ (cod = 1,5-cyclooctadiene) in the presence of weakly binding ligands, S, has proved to be an effective way of making the complexes $[IrH_2L_2S_2]^+$ (S = Me_2CO, tetrahydrofuran (thf), H_2O, MeI, and MeCN).[8] We therefore performed this reaction in the presence of 8-fluoroquinoline. The greenish white product was purified by recrystallization from CH_2Cl_2–Et_2O and characterized by IR and ^1H, ^{19}F, and ^{31}P NMR spectroscopy and, in particular, by an X-ray crystallographic study.

We will first discuss the spectral studies. The ^1H NMR spectrum of the product shows two hydride resonances, H_A at δ −19.5 and H_B at δ −39.3. Each shows coupling to two cis PPh_3 groups ($^2J(P,H(cis))$ = 16.5 Hz (H_A) and 15.3 Hz (H_B)) as appropriate for a cis arrangement of these ligands. The two hydrogens are present in the same molecule as shown by the H,H coupling ($^2J(H,H')$ = 10.3 Hz), as we often find in such complexes. Significantly, only H_B shows coupling to ^{19}F ($^2J(H,F(trans))$ = 95 Hz), suggesting that H_B is trans to F. Larger coupling between trans ligands is a common feature of transition-metal complexes,[9] but the rarity of hydrido fluorides[10] means that no cases of trans H,F coupling have been reported. The resonances for the PPh_3 and fluoroquinoline ligands are normal.

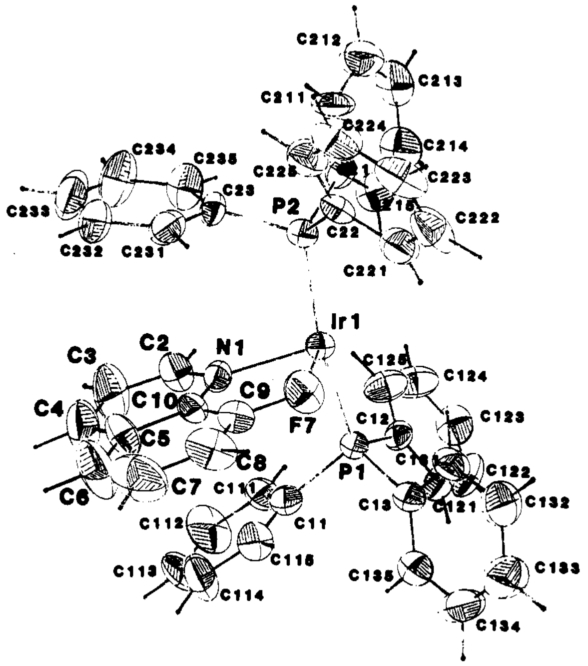

Figure 1.

Table I. Crystal Data for $IrSbP_2F_7NC_{45}H_{38}$[a]

formula	$IrSbP_2F_7NC_{45}H_{38}$	λ(Mo Kα)	0.71069 Å
M_r	1087.7	D_{calcd}	1.710 g cm^{-3}
a	11.904 (7) Å	Z	4
b	19.891 (11) Å	obsd reflcns	5114
c	18.213 (4) Å	R	5.5%
β	101.63 (4)°	R_w	7.0%
V	4223.9 (37) Å^3	space group	$P2_1/c$
F(000)	2116	scan rate	variable
μ(Mo Kα)	39.14 cm^{-1}	scan type	θ–2θ

[a] Obtained on a Syntex P3 diffractometer.

In acetone-d_6, the fluoroquinoline is displaced to give $[IrH_2L_2S_2]^+$ (S = Me_2CO), showing the high coordinative lability of the quinoline ligand. Conversely, the isolated acetone complex will react in CD_2Cl_2 with the fluoroquinoline to re-form the chelate complex.

The ^{19}F NMR spectrum shows a resonance centered at δ −172 from the $CFCl_3$ standard. The coupling to H_B is clearly resolved ($^2J(F,H)$ = 100 Hz), but for its exact value, we prefer to trust the ^1H NMR signal, which was better resolved. The chelated fluorine showed a coordination shift of −46 ppm relative to the resonance for free 8-fluoroquinoline at δ −126.

The IR spectrum of the complex shows a strong band at 1231.6 cm^{-1}, which we identify as the C–F stretching frequency. Aryl C–F vibrations have been reported in the range 1100–1250 cm^{-1}.[11] The coordination shift from free 8-fluoroquinoline (ν(C–F) = 1245.7 cm^{-1} (s)) is −14 cm^{-1}. The interaction therefore probably

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Table II. Positional Parameters for $IrSbP_2F_7NC_{45}H_{38}$[a]

atom	*x*	*y*	*z*
Ir1	0.81613 (4)	0.22977 (2)	0.08759 (2)
Sb1	0.8116 (1)	0.4704 (1)	0.2293 (1)
P1	0.6207 (3)	0.2369 (2)	0.0477 (2)
P2	1.0124 (3)	0.2366 (2)	0.1085 (2)
F1	0.8147 (13)	0.4200 (7)	0.3143 (7)
F2	0.9012 (15)	0.4079 (7)	0.1974 (9)
F3	0.6900 (15)	0.4225 (8)	0.1853 (11)
F4	0.9279 (11)	0.5157 (7)	0.2835 (12)
F5	0.7142 (10)	0.5313 (6)	0.2576 (7)
F6	0.7998 (18)	0.5192 (9)	0.1466 (9)
F7	0.8199 (6)	0.1041 (4)	0.1037 (4)
N1	0.8079 (8)	0.2054 (5)	0.2003 (5)
C2	0.8003 (13)	0.2527 (6)	0.2504 (7)
C3	0.7896 (18)	0.2412 (9)	0.3236 (9)
C4	0.7795 (16)	0.1762 (10)	0.3464 (8)
C5	0.7872 (12)	0.1240 (7)	0.2966 (7)
C6	0.7830 (18)	0.0568 (9)	0.3161 (9)
C7	0.7920 (16)	0.0062 (10)	0.2668 (12)
C8	0.8062 (12)	0.0238 (7)	0.1954 (9)
C9	0.8079 (10)	0.0893 (7)	0.1738 (7)
C10	0.8014 (10)	0.1409 (7)	0.2235 (7)
C11	0.5403 (10)	0.2369 (8)	0.1241 (7)
C111	0.5185 (13)	0.1788 (8)	0.1573 (8)
C112	0.4680 (16)	0.1799 (12)	0.2184 (9)
C113	0.4376 (15)	0.2393 (13)	0.2470 (10)
C114	0.4643 (16)	0.2950 (10)	0.2175 (10)
C115	0.5127 (11)	0.2983 (8)	0.1533 (8)
C12	0.5707 (9)	0.3127 (7)	−0.0062 (6)
C121	0.4672 (11)	0.3124 (8)	−0.0564 (7)
C122	0.4283 (14)	0.3701 (9)	−0.0943 (8)
C123	0.4890 (14)	0.4290 (9)	−0.0817 (9)
C124	0.5894 (13)	0.4292 (8)	−0.0297 (10)
C125	0.6302 (11)	0.3709 (7)	0.0082 (9)
C13	0.5615 (10)	0.1678 (7)	−0.0129 (7)
C131	0.6306 (11)	0.1362 (7)	−0.0551 (7)
C132	0.5879 (13)	0.0840 (8)	−0.1044 (8)
C133	0.4760 (14)	0.0644 (9)	−0.1104 (9)
C134	0.4105 (13)	0.0955 (9)	−0.0689 (9)
C135	0.4479 (12)	0.1455 (8)	−0.0212 (8)
C21	1.0721 (10)	0.3084 (6)	0.0677 (6)
C211	1.1884 (10)	0.3148 (8)	0.0779 (8)
C212	1.2358 (13)	0.3697 (9)	0.0461 (9)
C213	1.1663 (15)	0.4154 (7)	0.0059 (8)
C214	1.0505 (14)	0.4103 (8)	−0.0035 (9)
C215	1.0043 (13)	0.3556 (8)	0.0266 (8)
C22	1.0772 (10)	0.1644 (6)	0.0718 (6)
C221	1.0144 (11)	0.1342 (7)	0.0076 (8)
C222	1.0588 (14)	0.0775 (8)	−0.0223 (8)
C223	1.1609 (13)	0.0521 (7)	0.0118 (10)
C224	1.2245 (12)	0.0807 (8)	0.0746 (9)
C225	1.1802 (11)	0.1375 (7)	0.1038 (8)
C23	1.0785 (10)	0.2426 (6)	0.2073 (6)
C231	1.0872 (11)	0.1860 (7)	0.2522 (7)
C232	1.1174 (12)	0.1899 (9)	0.3294 (8)
C233	1.1416 (15)	0.2515 (10)	0.3628 (8)
C234	1.1309 (16)	0.3076 (9)	0.3185 (9)
C235	1.0988 (14)	0.3017 (7)	0.2422 (8)

[a] Standard deviations are given in parentheses.

Table III. Selected Bond Distances (Å) and Angles (deg) for $IrSBP_2F_7NC_{45}H_{38}$

Ir1–P1	2.297 (3)	P1–Ir1–P2	168.9 (1)
Ir1–P2	2.294 (3)	P1–Ir1–F7	95.2 (1)
Ir1–N1	2.130 (9)	P1–Ir1–N1	94.5 (2)
Ir1–F7	2.514 (8)	P2–Ir1–F7	92.6 (6)
N1–C2	1.32 (2)	P2–Ir1–N1	95.6 (2)
N1–C10	1.36 (2)	F7–Ir1–N1	70.4 (3)
C2–C3	1.38 (2)	Ir1–N1–C2	121.6 (8)
C3–C4	1.37 (3)	Ir1–N1–C10	122.0 (8)
C4–C5	1.39 (2)	Ir1–F7–C9	109.0 (7)
C5–C10	1.42 (2)	C10–N1–C2	116.2 (10)
C5–C6	1.38 (2)	N1–C2–C3	125.3 (13)
C6–C7	1.37 (3)	N1–C10–C5	122.7 (11)
C7–C8	1.39 (3)	N1–C10–C9	119.0 (11)
C8–C9	1.36 (2)	C2–C3–C4	118.6 (15)
C9–C10	1.38 (2)	C3–C4–C5	119.0 (15)
		C4–C5–C10	118.1 (13)
		C4–C5–C6	122.8 (14)
		C10–C5–C6	119.1 (13)
		C5–C6–C7	122.0 (17)
		C6–C7–C8	118.0 (17)
		C7–C8–C9	121.5 (15)
		C8–C9–F7	119.5 (12)
		C8–C9–C10	121.0 (13)
		F7–C9–C10	119.4 (12)
		C9–C10–C5	118.3 (12)

only slightly weakens the C–F bond.

The crystal structure confirms that the molecule has a stereochemistry similar to that of other $[IrH_2L_2S_2]^+$ complexes and that the fluoroquinoline is chelated via a C–F bond (see Figure 1, Tables I–III, and the supplementary material).

The CF–Ir distance of 2.514 (8) Å is intermediate in length between the sum of the covalent radii (1.25 + 0.64 = 1.89 Å) and the sum of the van der Waals radii[12] (1.9 (estimate) + 1.35 = 3.25 Å). Such intermediate distances are not often observed and suggest that the interaction is weaker than a full covalent bond. Alcock has discussed the phenomenon of "secondary bonding"[13] in the structures of main-group compounds. Secondary bonding has not been proposed for transition metals up to now.

Glusker has shown[14,15] that C–F···M distances in alkali-metal fluorocarboxylate salts are shorter than the sum of the van der Waals radii (e.g., 2.470 Å in sodium fluoropyruvate, where the appropriate sum of van der Waals radii is 3.05 Å).

Uson, Cotton, et al. have reported[6] that two Ag···F distances in a mixed Pt–Ag cluster containing perfluorophenyl groups are 2.60 (1) and 2.69 (1) Å. The corresponding angles as well as the ^{19}F NMR data were not reported.

The C–F–Ir angle of 109.0 (7)° is slightly larger than those seen in the halocarbon complexes we have previously studied.[1,2] This may be attributable to the smaller s–p energy gap in the first-row element, which would make sp^3 hybridization more facile, accounting for a C–X–M angle of 109°. It might be argued that the angle is imposed by the ligand geometry, and indeed Richards[16] has recently observed a similar C–F–M bonding in $[Ru(\eta^2\text{-}SC_6F_5)(\eta^1\text{-}SC_6F_5)(PMe_2Ph)_2]$, in which the M–F distance of 2.489 (6) Å resembles ours but the M–F–C angle is 117.3°. This suggests that the C–Hal–M angle is quite flexible, as might be expected for a weak interaction.

One could also argue that the geometry of the complex imposes a short CF···Ir distance that does not necessarily correspond to an attractive interaction. This objection can only be met satisfactorily with a crystal structure of a nonchelated 8-fluoroquinoline, no examples of which seem to be reported.[17] However, it seems to be a general principle of structural chemistry that it is usually easier for bond angles to open up than for nonbonded contacts to be substantially shorter (0.75 Å in this case) than the sum of the van der Waals radii. We therefore believe the CF–Ir interaction is attractive, although weakly so.

Another possibility for the bonding is that the attraction is coulombic, not covalent at all, and that the C–F–Ir bond is the analogue of the X–H···X hydrogen bond but with the opposite polarity. This possibility is probably best approached by a theoretical study, which we have not attempted.

The rest of the structure is normal, and there are no unusual contacts or interactions apparent. The recent work by ourselves[1,2]

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(17) we have prepared $PdCl_2L_2$ and $[Cp_2TiLOSO_2CF_3]OSO_2CF_3$ (L = 8-fluoroquinoline), which appear to be nonchelating from NMR evidence: Crabtree, R. H.; Kulawiec, R. J.; Luo, X.-L., unpublished observations, 1986.

and others[6] shows that fluorocarbon complexation, although weak, may be a common phenomenon in the coordination chemistry of fluorocarbons, at least for coordinatively unsaturated metal centers. The ^{19}F coordination shift and, in suitable cases, the observation of coupling with the coordinated C–*F* nucleus seem to be useful spectroscopic criteria of binding.

Experimental Section

General Considerations. All manipulations were performed under dry nitrogen by employing standard Schlenk techniques. Dichloromethane was distilled from CaH_2; ether was distilled from sodium benzophenone ketyl and stored under nitrogen over molecular sieves. $[(cod)Ir(PPh_3)_2]SbF_6$ was synthesized by a literature procedure.[18] 8-Fluoroquinoline was synthesized from *o*-fluoroaniline (Aldrich) by a modification of the Skraup reaction.[19]

Synthesis of $[IrH_2(PPh_3)_2(L)](SbF_6)$ (L = 8-Fluoroquinoline). A solution of (η^4-1,5-cyclooctadiene)bis(triphenylphosphine)iridium(I) hexafluoroantimonate (213 mg, 0.201 mmol) and 8-fluoroquinoline (29.6 mg, 0.201 mmol) in 20 mL of dry, degassed dichloromethane was cooled to 0 °C, and hydrogen was bubbled through for 40 min. The volume of the pale yellowish green solution was reduced in vacuo to 5 mL, and the product was precipitated by addition of 20 mL of ether. The resulting pale greenish white powder was collected on a fritted disk, washed with ether, and dried in vacuo: yield 168 mg (76%); mp 181 °C dec. The product can be purified by precipitation from a concentrated dichloromethane solution with diethyl ether.

Spectroscopy. ^1H NMR spectra were obtained on a JEOL FX-90Q or a Bruker WM 250 spectrometer; chemical shifts are reported in δ (ppm) relative to Me_4Si. ^{19}F NMR spectra were obtained on a Bruker 500-MHz instrument ($CFCl_3$ internal standard). ^{31}P NMR spectra were obtained on a Varian CFT-20 instrument (85% H_3PO_4 external standard). IR spectra were recorded on a Nicolet 5S-X Fourier transform instrument.

Crystallography. A crystal of $IrSbP_2F_7NC_{45}H_{38}$ gave the data shown in Table I. Data (9361 points) were collected at room temperature by using a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 60.0°. The intensities of 3 standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. Heavy-atom positions were located by using direct methods.[20] Least-squares refinement followed by a difference Fourier synthesis allowed location of the remainder of the non-hydrogen positions. Hydrogen atom positions were calculated by assuming a C–H bond length of 0.97 Å and were included in the final refinement with fixed isotropic thermal parameters. Positions of the Ir–*H* atoms were not apparent from a difference Fourier synthesis. Anomalous dispersion corrections were made for Ir, Sb, and P. Scattering factors were taken from Cromer and Mann.[21]

The final cycle of refinement minimized $(|F_o| - |F_c|)^2$ and led to a final agreement factors: $R = 5.5\%$, $R = 100(\sum|F_o| - |F_c|/\sum|F_o|)$. A weight equal to $1/|F|$ was introduced in the final cycles of refinement: $R_w = 7.0\%$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for funding.

Registry No. $[IrH_2(PPh_3)_2(L)](SbF_6)$ (L = 8-fluoroquinoline), 108970-14-5; $[Ir(COD)(PPh_3)_2](SbF_6)$, 91410-27-4.

Supplementary Material Available: Calculated H positions (Table S2) and anisotropic thermal parameters (Table S3) (3 pages); F_o vs. F_c values (Table S1) (68 pages). Ordering information is given on any current masthead page.

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An Unusual Example of Intramolecular Hydrogen Bonding in a Metal Carbonyl Cluster Compound. Synthesis and Crystal and Molecular Structure of $Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu\text{-}OH)_2(\mu_4\text{-}S)$

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Received December 12, 1986

It is well-known that compounds containing hydroxyl groups readily engage in hydrogen bonding to Lewis bases, B:.[1] Hydrogen bonding can play an important role in determining the overall structure, bonding and reactivity of the compounds involved.[1] In metal carbonyl cluster compounds, hydroxyl ligands invariably adopt bridging coordination modes.[2] We now wish to report that we have prepared and structurally characterized the new hexaruthenium cluster $Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu\text{-}OH)_2(\mu_4\text{-}S)$ (**1**), which has two bridging hydroxyl ligands and have obtained evidence for the existence of a significant intramolecular hydrogen bonding interaction between them.

$$\mathrm{B}{:}{-}{-}{-}\overset{\delta+}{\mathrm{H}}{-}\overset{\delta-}{\mathrm{O}}$$

Experimental Section

General Procedures and Materials. All reactions were performed under nitrogen atmosphere. $Ru_3(CO)_{12}$ was purchased from Strem Chemical Co. and was used as received. $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ was prepared as previously reported.[3]

TLC separations were performed in air on 0.25-mm Kieselgel 60 F_{254} (E. Merck) purchased from Bodman Chemicals. UV irradiation was performed by using an external high-pressure mercury lamp. IR spectra were recorded on a Nicolet 5 DXB FT IR spectrometer. UV-vis spectra were measured on a Cary 210 spectrophotometer. ^1H NMR spectra were run on IBM NR-80 and Bruker AM-300 spectrometers operating at 80 and 300 MHz, respectively. Elemental analyses were performed by MicAnal, Tucson, AZ.

Synthesis. A 50-mL THF solution of 30 mg (0.04 mmol) of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$, 31 mg (0.040 mmol) of $Ru_3(CO)_{12}$, and 20 μL of distilled water was irradiated for 6 h at 25 °C in the presence of a nitrogen purge. The brown solution was evaporated to dryness in vacuo, and the residue was extracted with CH_2Cl_2. The undissolved residue was dissolved in THF and cooled to −20 °C. This yielded 13 mg of $Ru_4(CO)_{11}(\mu_4\text{-}S)_2$ (34%).[3] The CH_2Cl_2 extract was chromatographed on a Florisil column with CH_2Cl_2 as solvent. A brown band and a blue band were separated. The brown band was further separated by TLC (hexane/CH_2Cl_2, v/v 75/25). This yielded the following compounds in order of elution: 19 mg of $Ru_3(CO)_{12}$ and 3 mg of $Ru_6(CO)_{17}(\mu_4\text{-}S)_2$ (12%).[4] The blue compound was recrystallized from CH_2Cl_2 at 0 °C to yield 5 mg of $Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu\text{-}OH)_2(\mu_4\text{-}S)$ (**1**) (8%). IR (ν(CO) in hexane): 2117 (vw), 2089 (s), 2051 (vs), 2042 (m), 2030 (w), 2020 (w), 1993 (w), 1876 (w) cm^{-1}. IR (ν(OH) in CD_2Cl_2): 3687 (m), 3602 (w) cm^{-1}. UV-vis (in CH_2Cl_2): λ_{max} 368 nm, ϵ 870; λ_{max} 679 nm, ϵ 5150. ^1H NMR (δ in toluene-d_8): −3.35 (s, 2 H). This resonance was not changed by cooling to −40 °C. Anal. Calcd for $Ru_6SO_{20}C_{18}H_2$: C, 18.37; H, 0.17. Found: C, 18.45; H, 0.33.

Crystallographic Analyses. Crystals of **1** were obtained by slow evaporation of solutions in CH_2Cl_2 solvent at 0 °C. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo $K\alpha$ radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the Molecular Structure Corp. TEXSAN structure solving program library. Neutral-atom scattering factors were obtained from the standard sources.[5a] Anomalous dispersion corrections

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