Octahedral perfluoroalkyl complexes of Ir(III) formed by oxidative addition of perfluoroalkyl iodides to Ir(acac)(CO)₂¹

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Abstract: Oxidative addition of primary, secondary, or benzylic perfluoroalkyl iodides (R_{F} –I) to the phosphine free Ir(I) precursor Ir(acac)(CO)**2 1** (acac = 2,4-pentanedionato) proceeds smoothly to afford octahedral Ir(III) products Ir(acac)(I)(R_{F})(CO)₂, A combination of X-ray crystallographic studies and solution spectroscopy shows that these products are the result of overall trans-addition of the C–I bond to iridium, probably a result of thermodynamic control; evidence for a kinetic product resulting from net cis-addition is obtained in one case. Treatment of the Ir(III) compounds with AgOTf (Tf = CF₃SO₃) illustrates that the iodo ligand is replaced by triflate with retention of stereochemistry at Ir. The resulting triflate complexes are inert to displacement by H₂O or H₂. The Ir(III) products exhibit very high CO stretching frequencies in the IR, indicating that the CO ligands may be non-classical. A quantitative estimation of the degree of backbonding to the CO ligands in these compounds, and a comparison of the π -acceptor properties of CO and fluoroalkyl ligands, is made using an approach based on Density Functional Theory (DFT) and Natural Bond Orbital analyses.

Key words: iridium, fluoroalkyl, oxidation, carbonyl, DFT.

Résumé : L'addition oxydante d'iodures primaires, secondaires ou benzyliques perfluoroalkylés (R_F –I) sur le précurseur Ir(I) sans phosphine, Ir(acac)(CO)₂ (1) (acac = 2,4-pentanedionato), s'effectue sans problème et elle conduit à la formation de produits Ir(III) octaédriques Ir(acac)((I)(R_F)(CO)₂. Des études cristallographiques par diffraction des rayons X et d'autres réalisées par spectroscopie en solution permettent de montrer que ces produits sont le résultat d'une addition nette *trans* de la liaison C–I sur l'iridium, probablement sous l'influence d'un contrôle thermodynamique; dans un cas, on a toutefois été en mesure de mettre en évidence d'un produit cinétique résultant d'une addition nette *cis*. Le traitement des composés Ir(III) avec du AgOTf (Tf = CF₃SO₃) permet d'illustrer que le ligand iodo est remplacé par le triflate avec rétention de la stéréochimie au niveau de l'iridium. Les complexes triflates qui en résultent sont inertes aux déplacements par l'eau ou l'hydrogène. Les produits Ir(III) présentent des spectres infrarouges dans lesquels les fréquences d'élongation du CO sont très élevées, ce qui suggère que les ligands CO ne sont pas classiques. Faisant appel à la théorie de la densité fonctionnelle et une analyse des orbitales de liaison naturelle, on a fait une évaluation quantitative du degré de retour de liaison vers les ligands CO dans ces composés ainsi qu'une comparaison des propriétés des ligands CO et fluoroalkyles comme accepteurs π .

Mots-clés : iridium, fluoroalkyle, oxydation, carbonyle, théorie de la densité fonctionnelle (TDF).

[Traduit par la Rédaction]

Introduction

The oxidative addition of carbon-halogen bonds to lowvalent transition metal complexes is a fundamental organometallic reaction that plays a key role in many useful catalytic transformations (1). An important example is the addition of CH₃I to *cis*-[MI₂(CO)₂]⁻ (M = Rh or Ir) in the carbonylation of methanol to form acetic acid (2–6). Corresponding oxidative addition of a large variety of substrates to square-planar d^8 complexes of platinum has also been a subject of great interest and the source of a great many significant contributions from the Puddephatt group over the

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Dedicated to Professor Richard J. Puddephatt in recognition of his outstanding contributions to inorganic and organometallic chemistry.

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past three decades, only representative examples of which are referenced here (7–27). Our group has had a longstanding interest in using analogous oxidative addition reactions of perfluoroalkyl iodides, based on reactions originally reported in the 1960s (28, 29), to prepare perfluoroalkyl complexes of the late transition metals, including iridium (30–32), rhodium (31–36), palladium (37, 38), and platinum (39–43).

The square-planar iridium(I) complex 1 (Scheme 1) (44) is a commercially available catalyst for anti-Markovnikov arylation of olefins and olefin isomerization (45) and has been broadly employed to prepare other organometallic complexes through ligand substitution (46, 47) or cluster formation (48, 49). Simple oxidative addition reactions to this 16-electron complex do not appear to have been reported. Here, we report syntheses, reactivity, and DFT studies of a series of new perfluoroalkyl iridium complexes, obtained by oxidative addition of 1 with perfluoroalkyl iodides, which have been characterized spectroscopically, and in some cases, crystallographically.

Results and discussion

Synthesis and molecular structure of 1

Despite being known for four decades and being a compound of some synthetic utility (vide supra), the molecular **Fig. 1.** ORTEP diagram of **1** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are presented in Table 2.



structure of 1 has apparently not been determined accurately. A search of the Cambridge Structure Database (50) revealed a single report (code ACRHCO) of a 12% structure with no deposited coordinates, resulting from a Ph.D. thesis (51). In our hands, when 1 was synthesized according to the reported method (52), good quality crystals were obtained and were subjected to a single-crystal X-ray diffraction study. An ORTEP is shown in Fig. 1, details of the crystal data are presented in Table 1, and selected bond lengths and angles for the coordination sphere of Ir are given in Table 2. The intramolecular structure is unremarkable, but the crystal packing diagram shown in Fig. 2 reveals the expected faceto-face stacking of the individual planar molecules to give a linear chain structure with an Ir-Ir separation of 3.192 Å. Despite the absence of a deposited crystal structure, several studies of phenomena resulting from intermolecular interactions in the solid-state structure of this molecule have already been reported (53-58).

Oxidative addition of perfluoroalkyl iodides to 1

Treatment of 1 with primary, secondary, and benzylic perfluoroalkyl iodides (R_F –I) in CH₂Cl₂ at room temperature afforded oxidative addition of the R_F –I bond to give the Ir(III) complexes 2–7 in excellent yields as shown in Scheme 1. Crystal structures were obtained for complexes 4 and 5; ORTEP diagrams are presented in Figs. 3 and 4, respectively, and details of the crystal data and structure determinations are presented in Table 1. Selected bond lengths and angles for the coordination sphere of Ir are given in Table 2.

The structures establish an approximate octahedral coordination around iridium, with the fluoroalkyl and iodo ligands mutually trans to each other. Analogous trans-stereochemistry for the oxidative addition of fluoroalkyl iodides to square-planar compounds has previously been observed in reactions of Pt(II) complexes (37, 42, 59).

As previously observed for Pd(II) (38) and other Ir(III) (30) complexes, the Ir– R_F bond length to the primary fluoroalkyl group in **4** [2.093(5) Å] is significantly shorter than that to the much bulkier (60) secondary fluoroalkyl in **5** [2.139(3) Å]. The Ir–C(O) bond lengths in **4** [1.893(5), 1.907(5) Å] and **5** [1.897(4), 1.900(4) Å] are slightly longer than those in the Ir(I) precursor **1** [1.856(10), 1.883(14) Å], while the Ir–O(acac) bond lengths in **4** [2.037(3), 2.037(3) Å] and **5** [2.031(2), 2.035(2) Å] are slightly shorter than those in **1** [2.053(6), 2.078(8) Å]; both these features are consistent with formal oxidation at iridium and less backbonding from Ir \rightarrow CO. A more quantitative discussion of the degree of backbonding to the CO ligands is presented later. The Ir–I bond lengths for **4** [2.7363(4) Å] and **5**

Table 1. Summary of crystallographic data for 1, 4, 5a, 8, 9, and 13.

Compound	1	4	5a	8	9	13
Formula	C ₇ H ₇ IrO ₄	C ₁₀ H ₇ F ₇ IIrO ₄	C ₁₀ H ₇ F ₇ IIrO ₄	C ₉ H ₇ F ₆ IrO ₇ S	C ₁₀ H ₇ F ₈ IrO ₇ S	C ₂₇ H ₂₂ F ₇ IIrO ₃ P
Formula mass	347.33	643.26	643.26	565.41	615.42	877.52
Space group	<i>P</i> -1	P2(1)/n	P2(1)/n	P2(1)/n	<i>P</i> -1	P2(1)/c
a (Å)	6.3387(15)	11.5266(12)	10.5998(12)	9.3487(10)	8.4781(8)	13.507(5)
b (Å)	7.6501(17)	11.9579(13	11.6832(13)	12.7522(14)	9.8173(10)	11.672(4)
<i>c</i> (Å)	9.102(2)	11.5760(12	13.2202(14)	12.9532(14)	11.5359(11)	18.783(6)
α (°)	106.776(3)	90	90	90	75.2520(10)	90
β (°)	90.686(3)	98.415(2)	110.084(2)	100.129(2)	76.5010(10)	106.124(6)
γ (°)	100.288(3)	90	90	90	67.5830(10)	90
V (Å ³)	414.83(17)	1593.9(3)	1537.6(3)	1520.2(3)	848.32(14)	2844.6(16)
Ζ	2	4	4	4	2	4
$D_{\text{calcd.}}$ (g cm ⁻³)	2.781	2.681	2.779	2.470	2.409	2.049
$\mu (mm^{-1})$	16.062	10.399	10.780	9.019	8.108	5.909
Temp. (K)	100(2)	173(2)	173(2)	208(2)	208(2)	208(2)
Diffractometer	Bruker Smart Apex CCD					
Radiation	Mo Kα (0.71073 Å)					
Crystal size (mm)	$0.50 \times 0.15 \times$	$0.10 \times 0.07 \times$	$0.15 \times 0.10 \times$	$0.29 \times 0.27 \times$	$0.33 \times 0.28 \times$	$0.40 \times 0.20 \times$
	0.05	0.05	0.10	0.25	0.18	0.20
<i>F</i> (000)	316	1168	1168	1056	576	1664
Measured reflns.	5325	13434	12862	9543	14067	19232
Independent reflns.	1519	3710	3595	3483	2967	6709
$R(F) (\%)^{a}$	0.0436	0.0303	0.0230	0.0324	0.0328	0.0511
$R(wF^2)$ (%) ^b	0.1058	0.0679	0.0525	0.0720	0.0804	0.1276

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$ ${}^{b}R(wF^{2}) = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}; w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP], P = [2F_{c}^{2} + \max(F_{o}, 0)] / 3.$

Table 2	. Selected	bond length	is (Å) and	angles (°)	for iridium	complexes.
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Compound	1	4	5a	8	9	13
Ir–R _F		2.093(5)	2.139(3)	2.039(5)	2.049(6)	2.076(8)
Ir–CO	1.856(10)	1.893(5)	1.897(4)	1.916(5)	1.919(6)	1.843(8)
	1.883(14)	1.907(5)	1.900(4)	1.917(5)	1.920(6)	_
Ir-O(acac)	2.053(6)	2.037(3)	2.031(2)	2.013(3)	2.016(4)	2.038(5)
	2.078(8)	2.037(3)	2.035(2)	2.014(3)	2.024(4)	2.225(6)
Ir–I		2.7363(4)	2.7205(3)		V	2.7202(8)
Ir–OTf	_	_	_	2.184(3)	2.154(4)	_
C _a -F	_	1.359(6)	1.398(4)	1.306(6)	1.356(8)	1.557(11)
	_	1.375(6)	_	1.316(6)	1.367(8)	1.369(8)
	_	_	_	1.326(6)	_	_
C _β –F	_	1.354(6)	1.338(4)	_	1.321(9)	1.402(12)
	_	1.342(6)	1.339(4)	_	1.352(8)	1.360(11)
	_	_	1.332(4)	_	1.300(9)	_
	—	_	1.338(4)	—	_	—
	—	_	1.337(4)	—	_	—
	—	_	1.329(4)	_	_	—
C–O (CO)	1.132(12)	1.131(6)	1.123(4)	1.118(6)	1.124(8)	1.139(9)
	1.105(15)	1.122(6)	1.125(4)	1.118(6)	1.120(7)	—
X–Ir–R _f	—	172.49(13)	173.67(8)	171.95(16)	172.7(2)	99.2(2)
C(O)– Ir – $C(O)$	89.2(5)	91.7(2)	92.63(14)	94.3(2)	91.7(2)	_
Ir–PPh ₃	_	_	_		—	2.3445(16)
PPh ₃ –Ir–I			_		—	168.49(4)

 $\left[2.7205(3)\ \text{\AA}\right]$ are essentially the same. As previously observed in Pd(II) complexes (38), the secondary α -C–F bond lengths in 4 [1.359(6), 1.375(6) Å] are shorter than the tertiary α -C-F bond length in 5 [1.398(4) Å].

Solution spectroscopy is also consistent with transstereochemistries for compounds 2-5a and 7. Observation of a single methyl resonance for the acac CH₃ groups is consistent with a structure having a plane of symmetry perpendicu**Fig. 2.** Packing diagram for **1** with ellipsoids drawn at the 30% probability level.



Fig. 3. ORTEP diagram of **4** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are presented in Table 2.



lar to the acac plane, and observation of symmetry equivalent α -CF₂ fluorines in 4 or β -CF₃ groups in 5a is only consistent with a plane of symmetry including the α -carbon of the fluoroalkyl group. Only the illustrated transstereochemistries satisfy both these requirements. The overall structure of compound 6 is not unambiguously defined by spectroscopy, as the stereocenter at the α -carbon precludes any symmetry planes, yet only one CH₃ group is observed for the acac ligand; we assume that this arises due to accidental isochronicity of these methyl resonances and that the structure of 6 is analogous to those of its relatives. Curiously, in the reaction of 1 with perfluoro-iso-propyl iodide, a second set of transient peaks was observed in the reaction mixture; only a single CF₃ resonance was observed in the ¹⁹F NMR spectrum and two methyl resonances were observed in the ¹H NMR spectrum. These observations are only consistent with the structure of this second compound being 5b (Scheme 1). These peaks disappear over a short **Fig. 4.** ORTEP diagram of **5a** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are presented in Table 2.



time, leaving **5a** as the only isolable product. This observation suggests that, at least in the case of perfluoro-*iso*-propyl iodide, the kinetic stereochemistry of oxidative addition is cis, and perhaps that in all cases described here, the final observed trans-stereochemistry may be the result of thermodynamic control. It is interesting to note that cis oxidative addition was reported in the oxidative addition of perfluoro*n*-propyl iodide to Rh(acac)L₂ (L = PPh₃, PMePh₂) to give compounds **14** (61) but that trans-stereochemistries are the demonstrable kinetically controlled norm for oxidative addition of perfluoroalkyl iodides to Pt(II) systems (37, 42).



14 (L = PPh_3 , $PMePh_2$)

We have shown previously that the iodide ligand in $Cp*Ir(PMe_3)(R_F)(I)$ compounds is easily substituted by treatment triflate on with AgOTf, to give $Cp*Ir(PMe_3)(R_F)(OTf)$ complexes, in which the triflate ligand can readily be substituted by water to give cationic Cp*Ir(PMe₃)(R_F)(OH₂)][OTf] compounds (32). These water compounds proved to be useful precursors for heterolytic activation of H₂, with subsequent hydrogenolysis of α -CF bonds to liberate hydrofluorocarbon products (62, 63). To see whether analogous reactivity could be observed in triflates derived from the systems described here, compounds 2-5a were treated with AgOTf in CH₂Cl₂ to afford the corresponding triflate analogues 8-11 (Scheme 1). Crystal structures of 8 and 9 were carried out; ORTEP diagrams are provided in Figs. 5 and 6, respectively. Crystallographic

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Fig. 5. ORTEP diagram of **8** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are presented in Table 2.



Fig. 6. ORTEP diagram of **9** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are presented in Table 2.



Fig. 7. ORTEP diagram of **13** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are presented in Table 2.



data are presented in Table 1 and selected bond lengths and angles in Table 2.

The crystal structures confirm the trans-stereochemistries of **8** and **9**, and solution NMR data are also consistent with this stereochemistry for all compounds **8–11**; replacement of iodide with triflate clearly proceeds via a mechanism in which overall stereochemistry at iridium is retained. However, no reaction of these compounds with either water or H₂ was observed, in contrast to our previous observations on pentamethylcyclopentadienyl analogues (62, 63) and in contrast with the observations of Eisenberg on dicationic Ir(III)– CF₃ complexes (64). Compounds **8–11** appear to possess the classic inertness expected for low spin d⁶ compounds of the third transition series.

Finally, **1** was treated with 1 equiv. of PPh₃ to prepare the phosphine analogue **12** (Scheme 1) according to the reported method (44). Treatment of **12** with perfluoro-*n*-propyl iodide resulted in smooth oxidative addition, but NMR spectroscopy of the reaction mixture showed the presence of two isomeric products whose relative concentration did not change with time. Crystallization afforded single crystals of the major isomer, whose structure was obtained by X-ray diffraction and shown to be **13** (Scheme 1). An ORTEP diagram is presented in Fig. 7; crystallographic details are in Table 1, and selected bond lengths and angles in Table 2. The structure shows the perfluoropropyl group cis to iodide and also cis to PPh₃, with these three ligands adopting a mutually meridional configuration. The structure of the minor isomer remains unknown.

Computational studies

The expected increase in the IR stretching frequencies of the CO ligands is observed on formation of compounds 2–7 from 1; values of v_{CO} are shown in Table 3. It is interesting to note that in the Ir(III)–iodo complexes 2–7, one of the CO stretching vibrations (v_{sym}) occurs at a value higher than that of free CO (2143 cm⁻¹), illustrating that in these phosphinedonor-free Ir(III) complexes, the CO ligands may be non-

Table 3. Values of v_{CO} (cm⁻¹ in CH₂Cl₂).

Compound	$v_{CO} (cm^{-1})$
1	2072, 1994
2	2150, 2106
3	2148, 2105
4	2145, 2103
5a	2149, 2104
6	2147, 2104
7	2147, 2104
8	2168, 2125
9	2167, 2125
10	2167, 2125
11	2169, 2129

classical (65–67), and that relatively little backbonding from Ir \rightarrow CO π^* may be present. Replacement of iodide by the more electronegative triflate ligand in compounds **8–11** increases v_{CO} even further, but there is no significant effect on the CO frequencies by changing the fluoroalkyl ligand structure (CF₃, primary, or secondary).

The advent of density functional theory (DFT) (68–71), natural bond orbital (NBO) (72, 73), and natural population analysis (NPA) (74) as powerful tools for probing electronic structure in main-group and transition metal compounds(75) led us to apply these methods to representative compounds discussed here.

Four compounds were studied by DFT/NBO. The structures of starting material 1, 2, 3, and 5a, containing representative CF₃, primary (C₂F₅) and secondary $[(CF_3)_2CF]$ ligands were optimized using the B3LYP functional with the LACV3P**++ basis set, as implemented in the Jaguar suite of programs(76); extended core potentials were used for Ir and I, with all other atoms treated using a 6-311G**++ basis set. For compounds 1 and 5a, this procedure reproduced the crystallographically determined bond lengths within 0.02 Å and angles within 1°. The computed structures were confirmed as energy minima by calculating the vibrational frequencies by second derivative analytic methods and confirming the absence of negative frequencies. The use of second-order perturbative NBO analysis for estimating metal-ligand backbonding interaction energies (ΔE_{bb}), obtained from the off-diagonal Fock matrix element expressed in the NBO basis, has been thoroughly described and is now well-established (77-79). In our molecules, appropriate values of $\Delta E_{\rm bb}$ reflect the energies of delocalization of the three formal "lone pairs" on Ir [the non-bonding d_{xy} , d_{xz} , and d_{yz} orbitals of d⁶ Ir(III) in the NBO analysis] into the π^* antibonding orbitals of the two CO ligands. Corresponding delocalization energies from the same metal orbital set into the C–F or C–C σ^* antibonding orbitals on the $\alpha\text{-carbon}$ of the fluoroalkyl ligand can likewise be obtained. These values of ΔE_{bb} for compounds 1, 2, 3, and 5a are presented in Table 4, which also tabulates the natural charges from the NPA on iridium and the CO ligand atoms arising from the NBO treatment (80).

The data in Table 4 clearly show that when square-planar 1 reacts with fluoroalkyl iodides to form the oxidative addition products, the iridium is indeed oxidized, with an approximate doubling of the positive charge at the metal

Table 4. NPA charges on Ir and CO ligands, and Ir–CO and Ir– R_F backbonding interaction energies (ΔE_{bb} kcal/mol).

Compound	1	2	3	5a
Ir \rightarrow C–O (π^*)	96.5	64.1	68.2	70.4
Ir $\rightarrow \alpha$ -C–F (σ^*)		6.5	4.9	2.5
Ir $\rightarrow \alpha$ -C–C (σ^*)		_	1.0	1.8
Total Ir $\rightarrow R_F (\sigma^*)$		6.5	5.9	4.3
Charge on Ir	+0.26	+0.50	+0.51	+0.52
Charge on CO (C)	+0.57	+0.65	+0.64	+0.64
Charge on CO (O)	-0.44	-0.38	-0.38	-0.38

center. The carbon atoms of the CO ligands become more positive while the corresponding O atoms become more negative, resulting in a more polar CO ligand relative to the corresponding situation in 1. This increase in positive charge on iridium results in a dramatic reduction in backbonding from Ir \rightarrow CO (π^*), illustrated by the loss of one third of the corresponding delocalization energy ($\Delta E_{\rm bb}$). The changes in formal charges on Ir and the CO ligand atoms are independent of the fluoroalkyl ligand. The fluoroalkyl ligands themselves are very weak π -acceptors compared to CO. The number of fluorines on the α -carbon dominates the extent of backbonding, with CF₃ being the best; replacement of the acceptor C-F (σ^*) orbitals with C-C (σ^*) orbitals results in progressively poorer π -acceptor properties. The relative π acceptor properties of CF3 and CO agree well with those recently reported for Mn and Tc carbonyl complexes (77), and it is clear that in a competition for backbonding with CO ligands, fluoroalkyl ligands fare poorly. We concur with other authors that the increase in CO stretching frequencies on oxidation of a metal center results from two factors: increased polarization of the C-O bond and reduced population of CO π^* antibonding orbitals (81).

Experimental

General data

Air-sensitive reactions were performed in oven-dried glassware using standard Schlenk techniques under an atmosphere of nitrogen, which was deoxygenated over BASF catalyst and dried over Aquasorb or in a Braun drybox. Methylene chloride, hexanes, diethyl ether, tetrahydrofuran, and toluene were dried over an alumina column under nitrogen (82). NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometer. ¹H NMR spectra were referenced to the protio impurity in the solvent: C_6D_6 (7.16 ppm), CD₂Cl₂ (5.32 ppm). ¹⁹F NMR spectra were referenced to external CFCl₃ (0.00 ppm). ¹³C{¹H} NMR spectra were referenced to the deuterium solvent. Coupling constants are reported in units of Hertz and are absolute values. IR spectra were recorded on a PerkinElmer FTIR 1600 Series spectrophotometer. Elemental analyses were performed by Schwartzkopf (Woodside, NY) and X-ray crystallographic analyses at the University of California, San Diego.

IrCl₃·xH₂O (Pressure Chemicals), Hacac and *sec*-C₄F₉–I (Alfa Aesar), AgOTf, and R_F–I (R_F = CF₃, C₂F₅, *n*-C₃F₇, *i*-C₃F₇, CF₂C₆F₅) (Synquest) were commercially available. Ir(acac)(CO)₂ (52) and Ir(acac)(CO)(PPh₃) (44) were prepared using literature procedures.

Computations

Structures were optimized at the DFT (B3LYP) level of theory, using ECP values on Ir and I atoms and a 6– 311G**++ basis set for all other atoms, as implemented by Jaguar, versions 6.5 and 7.0 (76). Optimized geometries are provided in the Supplementary Data.³ NPA (72–75) were carried out at the B3LYP level of theory using the NBO program (80), also implemented as part of the Jaguar suite. As part of the NBO program, second-order perturbation analysis was used to estimate metal–ligand backbonding energies (ΔE_{bb}) with the overall value obtained by summing all second-order perturbation E(2) terms between the relevant metal d-orbital donor lone pair and the appropriate π^* C–O or σ^* C–F or σ^* C–C acceptor orbitals

$Ir(CO)_2(acac)$ (1) (52)

IR (hexane, cm⁻¹): 2074, 1999; IR (CH₂Cl₂, cm⁻¹): 2072, 1994. ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ : 5.07 (s, H, CH), 1.54 (s, 6H, 2CH₃). Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/hexanes.

$Ir(CO)_2(acac)(CF_3)(I)$ (2)

CF₃I was bubbled into a yellow CH₂Cl₂ (15 mL) solution of Ir(CO)₂(acac) (174 mg, 0.500 mmol) for 5 s. The solution turned brown-red gradually, then back to yellow again. After 6 h, IR showed no peak for starting materials. The solvent was removed under vacuum to give a yellow solid, which was crystallized from CH₂Cl₂/hexane at -30 °C to give yellow crystals (230 mg, 86%). IR (CH₂Cl₂, cm⁻¹): 2150 (s), 2106 (vs). ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ : 5.10 (H, s, CH), 1.53 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 470 MHz, 25 °C) δ : -22.4 (F, s, CF₃). Anal. calcd. for C₈H₇F₃IIrO₄ (%): C 17.69, H 1.30; found (%): C 17.77, H 1.38.

$Ir(CO)_2(acac)(CF_2CF_3)(I)$ (3)

C₂F₅I was bubbled into a yellow CH₂Cl₂ (15 mL) solution of Ir(CO)₂(acac) (87 mg, 0.250 mmol) for 5 s. The solution turned brown-red gradually, and was allowed to react overnight to give a brown solution. IR showed the reaction had finished. The solvent was removed under vacuum to give a brown solid, which was crystallized from CH₂Cl₂/hexane at -30 °C to give a yellow crystalline solid (128 mg, 86%). IR (CH₂Cl₂, cm⁻¹): 2148 (s), 2105 (vs). ¹H NMR (C₆D₆, 300 MHz, 25 °C) δ : 5.11 (H, s, CH), 1.54 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 282.2 MHz, 25 °C) δ : -83.7 (s), -91.0 (s). Anal. calcd. for C₉H₇F₅IIrO₄ (%): C 18.22, H 1.19; found (%): C 18.82, H 1.07.

$Ir(CO)_2(acac)(CF_2CF_2CF_3)(I)$ (4)

To a yellow CH₂Cl₂ (20 mL) solution of Ir(CO)₂(acac) (274 mg, 0.790 mmol) was added *n*-C₃F₇–I (0.11 mL, 0.79 mmol) at 0 °C. The colour turned to yellow \rightarrow orange \rightarrow yellow over 5 min. After 4.5 h, ¹⁹F NMR showed some residual peaks for *n*-C₃F₇–I, and the mixture was allowed to

react overnight to give a light yellow solution. The solvent was removed to give a light orange-yellow solid, which was crystallized from CH₂Cl₂/hexane at -30 °C to give a yellow crystalline solid (439 mg, 86%). The solid was recrystallized from ether/hexane at -60 °C to give crystals suitable for X-ray diffraction. IR (hexane, cm⁻¹): 2145 (s), 2103 (s). ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ : 5.09 (H, s, CH), 1.52 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 470 MHz, 25 °C) δ : -79.3 (3F, t, ³J_{FF} = 11 Hz, CF₃); -89.3 (2F, q, ³J_{FF} = 11 Hz, α -CF₂); -118.7 (2F, s, β -CF₂). Anal. calcd. for C₁₀H₇F₇IIrO₄ (%): C 18.67, H 1.10; found: C 18.84, H 1.22.

$Ir(CO)_2(acac)[CF(CF_3)_2](I)$ (5a, 5b)

To a yellow CH₂Cl₂ (20 mL) solution of $Ir(CO)_2(acac)$ (204 mg, 0.600 mmol) was added *i*-C₃F₇–I (0.09 mL, 0.6 mmol) at 0 °C. There was no apparent colour change, and the mixture was allowed to react overnight to give a light yellow solution. IR showed no peak for starting materials, and two sets of ¹H and ¹⁹F NMR signals, corresponding to two product isomers **5a** (major) and **5b** (minor) were observed. On standing at room temperature, the mixture evolved to give only **5a**. The solvent was removed to give a yellow solid (292 mg, 82%), which was recrystallized from ether/hexane at –60 °C to give crystals suitable for X-ray diffraction.

5a

IR (hexane, cm⁻¹): 2145 (s), 2103 (s); IR (CH₂Cl₂, cm⁻¹): 2149 (s), 2104 (s). ¹H NMR (C₆D₆, 500 MHz, 25 °C) 5.04 (H, s, CH), 1.51 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 470 Hz, 25 °C) δ : -71.0 (d, 6F, ³J_{FF} = 10 Hz, CF₃), -166.8 (sept, 1F, ³J_{FF} = 10 Hz, CF).

5b

¹H NMR (C₆D₆, 500 MHz, 25 °C) 5.14 (H, s, CH), 1.54 (3H, s, CH₃), 1.49 (3H, s, CH₃). ¹⁹F NMR (C₆D₆, 470 Hz, 25 °C) δ : -70.5 (6F, d, ³*J*_{FF} = 10 Hz, CF₃), -179.8 (1F, sept, ³*J*_{FF} = 10 Hz, CF).

Anal. calcd. for $C_{10}H_7IIrF_7O_4$ (%): C 18.67, H 1.10; found: C 18.74, H 1.20.

$Ir(CO)_2(acac)[CF(CF_3)(CF_2CF_3)](I)$ (6)

To a CH₂Cl₂ (30 mL) solution of Ir(CO)₂(acac) (34.7 mg, 0.1 mmol) was added *sec*-C₄F₉I (0.02 mL), and an immediate colour change from yellow to orange was observed. The mixture was stirred at room temperature for 2 h, and the solvent was removed to give a yellow-orange solid, which was recrystallized from CH₂Cl₂/hexane at -30 °C to give a yellow crystalline solid (253 mg, 76%). IR (CH₂Cl₂, cm⁻¹): 2147 (s), 2104 (s). ¹H NMR (C₆D₆, 300 MHz, 25 °C) δ : 5.01 (1H, s, CH), 1.49 (6H, s, CH₃). ¹⁹F NMR (C₆D₆, 282 MHz, 25 °C) δ : -69.67 (3F, s, γ -CF₃); -79.41 (3F, s, β -CF₃); -106.3 (F, d, ²J_{FF} = 302 Hz, CF_A); -111.4 (F, d, ²J_{FF} = 302

³Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3803. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC numbers 685793–685798 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Hz, CF_B); -169.22 (F, s, CF). Anal. calcd. for $C_{11}H_7F_9IIrO_4$ (%): C 19.06, H 1.02; found: C 19.46, H 1.44.

$Ir(CO)_2(acac)(CF_2C_6F_5)(I)$ (7)

To a CH₂Cl₂ (30 mL) solution of Ir(CO)₂(acac) (56 mg, 0.16 mmol) was added C₇F₇I (0.03 mL), and an immediate colour change from yellow to orange was observed. The mixture was stirred at room temperature for 2 h, and the solvent was removed to give a yellow-orange solid, which was recrystallized from CH₂Cl₂/hexane at -30 °C to give a yellow crystalline solid (34 mg, 75%). IR (CH₂Cl₂, cm⁻¹): 2147 (s), 2104 (s). ¹H NMR (C₆D₆, 300 MHz, 25 °C) δ : 4.66 (1H, s, CH), 1.29 (6H, s, CH₃). ¹⁹F NMR (C₆D₆, 282 MHz, 25 °C) δ : -37.62 (2F, s, CF₂); -141.4 (2F, s, *o*-CF); -149.9 (F, s, *p*-CF); -161.1 (2F, s, *m*-CF). Anal. calcd. for C₁₄H₇F₇IIrO₄ (%) C 24.32, H 1.02; found (%): C, 24.76, H 1.34.

$Ir(CO)_2(acac)(CF_3)(OTf)$ (8)

To a CH₂Cl₂ (10 mL) suspension of AgOTf (104 mg, 0.405 mmol) was added a yellow CH₂Cl₂ (10 mL) solution of Ir(CO)₂(acac)(CF₃)(I) (200 mg, 0.368 mmol) at room temperature. The solution was stirred overnight to give a yellow solution and yellow precipitate. The solution was filtered to give a pale yellow solution. The solvent was removed under vacuum to give a white solid with some dark brown impurities, which was recrystallized by CH₂Cl₂/hexane to give yellow crystals suitable for X-ray diffraction (182 mg, 87%). IR (CH₂Cl₂, cm⁻¹): 2168 (s), 2125 (vs). ¹H NMR (C₆D₆, 300 MHz, 25 °C) δ : 5.02 (H, s, CH), 1.48 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 282 MHz, 25 °C) δ : -15.5 (3F, s, CF₃), -77.3 (3F, s, OTf). Anal. calcd. for C₉H₇F₆IrO₇S (%): C 19.12, H 1.25; found (%): C 19.54, H 1.66.

$Ir(CO)_2(acac)(CF_2CF_3)(OTf)$ (9)

To a CH₂Cl₂ (5 mL) suspension of AgOTf (130 mg, 0.510 mmol) was added a CH₂Cl₂ (10 mL) solution of Ir(CO)₂(acac)(C₂F₅)(I) (260 mg, 0.440 mmol) at room temperature. The white AgOTf turned quickly to a brownyellow solid, and after 1 h the solution was filtered to give a yellow solution. The solvent was removed to give a yellow solid, which was recrystallized from CH₂Cl₂/hexane at -30 °C to give yellow crystals suitable for X-ray diffraction (220 mg, 86%). IR (CH₂Cl₂, cm⁻¹): 2167 (s), 2125 (vs). ¹H NMR (C₆D₆, 300 MHz, 25 °C) δ : 5.03 (H, s, CH), 1.53 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 282 MHz, 25 °C) δ : -77.3 (3F, s, CF₃), -78.0 (3F, s, OTf), -83.6 (2F, s, CF₂). Anal. calcd. for C₁₀H₇F₈IrO₇S (%): C 19.52, H 1.15; found (%): C 19.64, H 1.21.

$Ir(CO)_2(acac)(CF_2CF_2CF_3)(OTf)$ (10)

Ir(CO)₂(I)(*n*-C₃F₇)(acac) (221 mg, 0.343 mmol) and AgOTf (106 mg, 0.412 mmol) were stirred in CH₂Cl₂ (15 mL) overnight to give a pale yellow solution with a pale yellow precipitate, which was filtered to give a yellow solution. The solvent was removed to give a yellow solid, which was recrystallized from CH₂Cl₂/hexane at -30 °C to give yellow crystals (206 mg, 91%). IR (CH₂Cl₂, cm⁻¹): 2167 (s), 2125 (s). ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ : 5.03 (H, s, CH), 1.53 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 470 MHz, 25 °C) δ : -76.9 (d, ⁴J_{FF} = 11 Hz, α-CF₂), -77.3 (3F, s, OTf), -79.6 (3F, t, ${}^{4}J_{FF}$ = 11 Hz, CF₃), -119.3 (2F, s, β-CF₂). Anal. calcd. for C₁₁H₇F₁₀IrO₇S (%): C 19.85, H 1.06; found (%): C 20.20, H 1.11.

$Ir(CO)_2(acac)[(CF(CF_3)_2](OTf) (11)$

A mixture of $Ir(CO)_2(I)(i-C_3F_7)(acac)$ (214 mg, 0.333 mmol) and AgOTf (100 mg, 0.33 mmol) was stirred in CH₂Cl₂ (15 mL) overnight to give a pale yellow solution with pale yellow precipitate, which was filtered to give a yellow solution. The solvent was reervystallized from CH₂Cl₂/hexane at -30 °C to give yellow crystals. IR (CH₂Cl₂, cm⁻¹): 2169 (s), 2129 (s). ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ : 4.87 (H, s, CH), 1.47 (6H, s, 2CH₃). ¹⁹F NMR (C₆D₆, 470 MHz, 25 °C) δ : -70.7 (6F, d, ³J_{FF} = 9 Hz, 2CF₃), -77.1 (3F, s, OTf), -145.7 (F, hept, ³J_{FF} = 9 Hz, CF). Anal. calcd. for C₁₁H₇F₁₀IrO₇S (%): C 19.85, H 1.06; found (%): C 19.64, H 1.30.

$Ir(CO)(PPh_3)(acac)(CF_2CF_2CF_3)(I)$ (13)

To a yellow CH_2Cl_2 (10 mL) solution of Ir(CO)(PPh₃)(acac) (50 mg, 0.086 mmol) was added excess $n-C_3F_7-I$ (0.05 mL, 0.38 mmol) at 0 °C. The reaction was monitored by ¹⁹F NMR and IR. After 90 minutes, ¹⁹F NMR showed two sets of peaks for two different isomers. IR (CH₂Cl₂) showed no peak for Ir(CO)(PPh₃)(acac). The solvent was removed under vacuum to give a yellow solid, which was recrystallized through slow evaporation from hexane/ether solution to give crystals of the major isomer (70 mg, 93%).

Major

IR (CH₂Cl₂, cm⁻¹): 2063 (s). ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ : 7.58–7.41 (15H, m, PPh₃), 5.09 (H, s, CH), 1.70 (3H, s, CH₃), 1.67 (3H, s, CH₃). ¹⁹F NMR (C₆D₆, 470 Hz, 25 °C) δ : -67.6 (F, mq, $J_{FF} = 264$ Hz, α -F), -72.6 (F, mq, ² $J_{FF} = 264$ Hz, α -F), -80.0 (3F, t, ³ $J_{FF} = 13$ Hz, CF₃), -112.7 (F, mq, ² $J_{FF} = 282$ Hz, β -F), -114.6 (F, mq, ² $J_{FF} = 282$ Hz, β -F). ³¹P{¹H} NMR (CD₂Cl₂, 202 MHz, 25 °C) δ : -4.89 (P, d, ³ $J_{PF} = 34$ Hz, PPh₃).

Minor

IR (CH₂Cl₂, cm⁻¹): 2063 (s). ¹H NMR (C₆D₆, 500 MHz, 25 °C) δ: 7.90–7.81 (15H, m, PPh₃), 5.71 (H, s, CH), 2.03 (3H, s, CH₃), 1.98 (3H, s, CH₃). ¹⁹F NMR (C₆D₆, 470 MHz, 25 °C) δ: -71.4 (F, mq, ²J_{FF} = 265 Hz, α-F), -93.4 (F, mq, ²J_{FF} = 265 Hz, α-F), -80.2 (3F, t, ³J_{FF} = 11 Hz, CF₃), -117.5 (F, mq, ²J_{FF} = 288 Hz, β-F), -122.2 (F, mq, ²J_{FF} = 289 Hz, β-F). ³¹P{¹H} NMR (CD₂Cl₂, 202 MHz, 25 °C) δ: -17.4 (P, d, ³J_{PF} = 24 Hz, PPh₃). Anal. calcd. for C₂₇H₂₂F₇IIrO₃P (%): C 36.95, H 2.53; found (%): C 37.27, H 3.17.

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