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Synthesis and structural studies of perfluoroalkyl-rhodium and iridium(III) compounds containing tris(pyrazolyl)borate ligands

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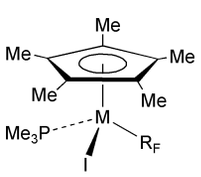
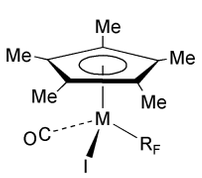
Oxidative addition of perfluorobenzyl iodide to $TpRh(C_2H_4)_2$ [Tp = tris(pyrazolyl)borate] affords $TpRh(CF_2C_6F_5)(C_2H_4)I$, from which the ethylene ligand can be displaced by CO to afford $TpRh(CF_2C_6F_5)(CO)I$. Similar reaction of perfluorobenzyl iodide with $TpIr(CO)_2$ or $Tp^*M(CO)_2$ [Tp* = tris(3,5-dimethylpyrazolyl)borate; M = Rh, Ir] affords $Tp^*M(CF_2C_6F_5)(CO)I$. Displacement of CO from the carbonyl complexes using PMe_3 is not clean and yields a mixture of compounds. However, displacement of ethylene from $TpRh(CF_2C_6F_5)(C_2H_4)I$ using PMe_3 cleanly affords $TpRh(CF_2C_6F_5)(PMe_3)I$. Similar oxidative addition reactions of perfluoro-n-propyl iodide afford $TpIr(C_3F_7)(CO)I$, $TpRh(C_3F_7)(CO)I$, $Tp^*Rh(C_3F_7)(CO)I$, $Tp^*Rh(C_3F_7)(PMe_3)I$, and $TpM(C_3F_7)(C_2H_4)I$ [M = Rh, Ir]. While displacement of ethylene from $TpRh(C_3F_7)(C_2H_4)I$ by PMe_3, to give $TpRh(C_3F_7)(PMe_3)I$ is facile, the corresponding reaction of the iridium analogue affords the salt $[TpM(C_3F_7)(C_2H_4)(PMe_3)]^+I^-$. Ethylene rotation barriers and Co stretching frequencies in these compounds are discussed. The molecular structures of $TpIr(CF_2C_6F_5)(CO)I$, $TpRh(CF_2C_6F_5)(PMe_3)I$, and $TpRh(C_3F_7)(PMe_3)I$ have been determined, and are also discussed in detail.

Introduction

Transition metal-fluoroalkyl complexes have been known since the early days of organometallic chemistry, yet, compared to their hydrocarbon analogues, their chemistry is relatively unexplored. We have been interested in syntheses and structures of fluoroalkyl complexes of the late transition metals, in part because of recent recognition of the lability of the α-fluorines in many such complexes towards a variety of carbon–fluorine bond activation reactions. In the case of Group 9 complexes, all the compounds we have studied thus far have been derivatives of the general precursors $Cp^*M(PMe_3)(R_F)I$ (**1**), formed by oxidative addition of R_FI to $Cp^*M(CO)_2$ to give $Cp^*M(CO)(R_F)I$ (**2**), followed by substitution of CO by PMe_3.[1–5]



1 M = Rh, Ir



2 M = Rh, Ir

Tris(pyrazolyl)borate ligands, first prepared by Trofimenko in 1966,[6] are similar to cyclopentadienyl ligands, in that they are tridentate anionic 6-electron donors that occupy three facial coordination sites.[7] Subsequently, a large variety of tris(pyrazolyl)borate metal complexes with different substituents on the pyrazolyl rings have been synthesized.[8–10] Abbreviations include Tp for tris(pyrazolyl)borate, and Tp* for the corresponding tris(3,5-dimethylpyrazolyl)borate analogue, by analogy with Cp and Cp*, abbreviations commonly used for cyclopentadienyl and its pentamethyl analogue.

With their larger cone angles (Cp: 150°, Cp*: 182°, Tp: 199°, Tp*: 236°),[11] tris(pyrazolyl)borates are thought to be more sterically demanding than their cyclopentadienyl analogues. In addition, they can bind as bidentate (κ^2) or tridentate (κ^3) ligands,[8–10,12,13] leading to the potential for formation of 16- or 18-electron complexes of a d^8 metal.[14–17] Changes in the pyrazole substituents can lead to a preference of one coordination mode over the other. For example the X-ray structure of $Tp^*Rh(CN\text{-}neopentyl)_2$ shows κ^2 coordination,[14] whereas Tp′Rh(NBD) (Tp′ = HB(3-Mepz)$_3$) shows κ^3 coordination.[16] In addition NMR and IR analysis of a solution of $Tp^*Rh(CN\text{-}neopentyl)_2$ also shows only κ^2-coordination, whereas for Tp′Rh(NBD) both κ^2- and κ^3-species appear to be present in solution.[14]

Reports of tris(pyrazolyl)borate complexes of Group 9 metals containing fluoroalkyl ligands are rare. The only examples appear to be $CpCo(\kappa^2\text{-}Tp)R_F$, formed by reaction of $CpCo(CO)R_F(I)$ and KTp (complexes were also formed using analogous bis and tetrakis(pyrazolyl)borates),[18] and a tetrakis(pyrazolyl)borate complex of rhodium formed by reaction of $[B(pz)_4]_2Rh_2(CO)_3$ with C_3F_7I, characterized only by microanalysis and IR spectroscopy.[19]

Given the dearth of examples we set out to prepare Tp and Tp* complexes of rhodium and iridium containing fluoroalkyl ligands, and to more thoroughly characterize their structural parameters in comparison with their known pentamethylcyclopentadienyl relatives **1** and **2**.

Results and discussion

Fluoroalkyl complexes of rhodium and iridium containing Cp* ligands of general structure **2**, containing Cp* ligands, can be prepared easily by oxidative addition of fluoroalkyl iodides (R_FI) to the readily available starting materials $Cp^*M(CO)_2$ [M = Rh, Ir]. The CO ligand can then be displaced by PMe_3 to afford complexes **1**.[1–5] Analogous starting materials $Tp^*M(CO)_2$ are available for both Rh[20] and Ir,[21] but for the Tp analogues, only $TpIr(CO)_2$ is known.[22] The analogous Rh complex appears to lose CO to give a sparingly soluble

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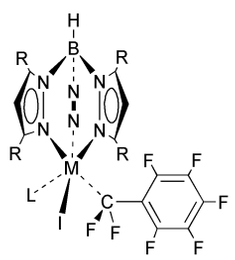
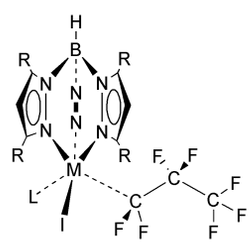
dinuclear complex $Tp_2Rh_2(CO)_3$, which is not a good substrate for oxidative addition reactions.[23] Fortunately, the corresponding ethylene complexes $TpM(C_2H_4)_2$ [M = Rh,[24] Ir[22,25]] are known, and we have used them as starting materials en route to the desired CO and PMe_3 complexes.

Reaction of $TpIr(CO)_2$ with perfluorobenzyl iodide affords the oxidative addition product **3**. The complex was characterized by a single crystal X-ray diffraction study, which confirmed the overall molecular connectivity shown. Detailed discussion of the structure and comparison with others is deferred until later. The solution structure is consistent with the solid state structure, as evidenced by spectroscopic studies. A characteristic single high frequency CO stretch is observed at 2085 cm^{-1} in the solution (CH_2Cl_2) IR spectrum. The ^1H NMR spectrum of **3** shows the expected nine resonances for the Tp protons, characteristic of the absence of any symmetry elements in the molecule. The ^{19}F NMR spectrum shows strongly coupled doublet resonances for the diastereotopic CF_2 fluorines, and a 2 : 1 : 2 pattern for the aromatic fluorines. Unlike corresponding Cp* derivatives, in which the ortho-fluorines are sharp, those of **3** are broad, and on lowering the temperature they decoalesce into two peaks, as do the corresponding meta-fluorines. This behavior is consistent with slowing of the rotation about the C_6F_5–CF_2 bond. A computer simulated full line shape analysis afforded a value of $\Delta G^{\ddagger} = 10.1 \pm 1.9$ kcal mol^{-1} for this process.



3 M = Ir, L = CO, R = H
5 M = Rh, L = CO, R = Me
11 M = Rh, L = CO, R = H
12 M = Rh, L = PMe_3, R = H



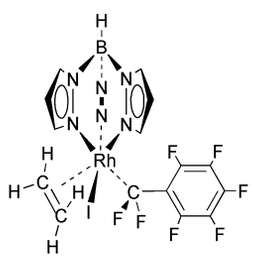
4 M = Ir, L = CO, R = H
6 M = Rh, L = CO, R = Me
14 M = Rh, L = CO, R = H
15 M = Rh, L = PMe_3, R = H

A similar reaction of $TpIr(CO)_2$ with perfluoro-n-propyl iodide afforded the analogous complex **4**. For **4**, the ^1H NMR shows signals for the nine Tp protons, consistent with the formation of a six coordinate complex. Four of the protons in the 3,5-positions on the pyrazole rings appear as doublets, with the other two having an additional small ($^5J_{HF} = 0.5$ Hz) coupling to a single fluorine. The magnitude is typical of five bond H–F couplings,[26] this same coupling is not seen for the perfluorobenzyl complex. The ^{19}F NMR spectrum of **4** shows separate, strongly coupled signals for the diastereotopic α-CF_2 fluorines, with an analogous set of peaks for the diastereotopic β-CF_2 fluorines. All of the coupling constants within the fluoroalkyl group were fully assigned by NMR simulation, and are listed in the experimental section.

Likewise, addition of perfluorobenzyl iodide to $Tp^*Rh(CO)_2$, or perfluoro-n-propyl iodide to $Tp^*Rh(CO)_2$, afforded excellent yields of the corresponding complexes **5** and **6**, characterized by their spectroscopic features. Each complex exhibited a single CO stretching frequency in the IR spectrum, the expected six methyl resonances and three pyrazole peaks in their ^1H NMR spectra, and the expected pattern of diastereotopic CF_2 fluorines in their ^{19}F NMR spectra. Unlike the Tp complex **3**, the perfluorobenzyl-rhodium complex **5** exhibited a ^{19}F NMR spectrum in which the ortho-fluorine resonances of are *sharp*, indicating that rotation about the CF_2–C_6F_5 bond is fast on the NMR timescale, a surprising observation considering the presence of a much bulkier Tp* ligand in **5**. Unfortunately, attempts to grow suitable X-ray quality crystals of any of the Tp* complexes were unsuccessful.

Unlike the clean substitution reactions observed for Cp* analogues, treatment of complexes **4**–**6** with PMe_3 afforded a mixture of several components that could not be characterized. Alternative routes to some phosphine derivatives are described below.

With the unavailability of $TpRh(CO)_2$ as a precursor for TpRh-fluoroalkyl complexes (*vide supra*), reactions of the corresponding $TpRh(C_2H_4)_2$ precursor were examined. Unlike the CO analogue above, reaction of $TpRh(C_2H_4)_2$ and perfluorobenzyl iodide in benzene at room temperature afforded a mixture of unidentifiable products. In contrast, when the reaction was carried out in THF solution, a single product was initially observed at low temperature (−70 °C) with concomitant release of one molecule of ethylene. As the reaction mixture gradually warmed, a second product was formed in a 1 : 1 ratio with the initial product. Removing the solvent under vacuum resulted in extensive decomposition, but the second product **7** could be isolated in low yields by precipitating it out of the reaction mixture with hexanes. Compound **7** was characterized by ^1H, ^{19}F NMR and IR. The IR spectrum showed the expected B–H stretch from the Tp ligand at 2498 cm^{-1}, and the ^1H NMR spectrum showed the expected nine pyrazole proton resonances, along with ethylene resonances as two broad peaks at δ 2.33 (2H) and 0.75 (2H). Observation of two peaks is indicative of an ethylene ligand freely rotating about the Rh–ethylene bond axis on the NMR timescale; a static ethylene bound to the stereogenic metal center in **7** would give rise to four inequivalent proton environments, while rotation about the M–ethylene axis affords pairwise exchange of mutually trans-environments only. Facile ethylene rotation is not unexpected, as the metal fragment to which the ethylene is bound is a d^6 ML_5 fragment.[27] Analogous observations regarding ethylene rotation have been made for neutral analogues $TpRe(CO)L(\eta^2\text{-}C_2H_4)$ [L = ^{t}BuNC, PMe_3, pyridine, 1-methylimidazole or NH_3),[28] and further study of this fluxional process in our system was not undertaken. The ^{19}F NMR spectrum of **7** shows the ortho-fluorines as an unusually broad peak, perhaps due to hindered rotation about the CF_2–C_6F_5 bond (*vide supra*) but this process was not examined further.



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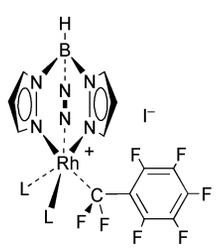
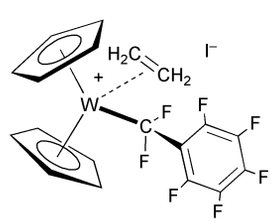


8 L = C_2H_4



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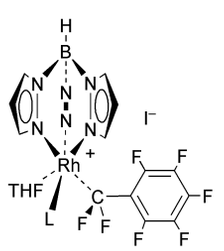
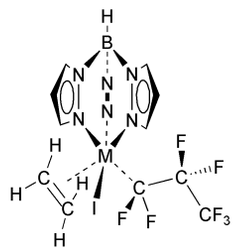


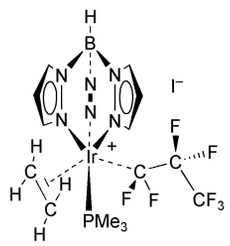
10 L = C_2H_4

While the structure of the initial product formed in this reaction is not known, some constructive speculation can be made concerning its structure. The NMR spectra of this compound exhibit nine pyrazole protons, diastereotopic CF_2 fluorines, and resonances due to a single bound ethylene. A resonance due to one dissociated ethylene molecule is also observed. Since the C_6F_5 fluorine resonances appear

unperturbed, we exclude the possibility of an η^3-benzyl ligand. Oxidative addition of R_FI to $TpRh(C_2H_4)_2$ probably proceeds *via* an initial electron transfer to give $[TpRh(C_2H_4)_2]^{+\bullet}$, I^- and $R_F^{\bullet}$, followed by recombination of the radical centers to give a cation **8**; an analogous pathway has been observed in reactions of $Cp_2W(C_2H_4)$ with perfluorobenzyl iodide to give **9**. This cation cannot be the species observed in solution, as it contains two molecules of coordinated ethylene, and too high a symmetry to be consistent with the NMR data. Loss of ethylene in THF probably affords the solvent complex **10** at low temperatures, and on warming this comes to equilibrium with the iodo complex **7**. While this method does not afford a clean route to either **10** or **7**, the mixture formed can be transformed into other useful complexes.



13 M = Rh
16 M = Ir



17

Treatment of a pure sample of **7**, or a mixture with **10** formed *in situ* as described above, with CO afforded the carbonyl derivative **11**, the rhodium analogue of **3**. Compound **11** is characterized by a single high frequency IR band at 2113 cm^{-1} (CH_2Cl_2), and ^1H and ^{19}F NMR spectra analogous to those of **3**, including the unusually broad resonance corresponding to the ortho fluorine substituents.

Furthermore, treatment of a mixture of **7** and **10** with PMe_3 resulted in displacement of ethylene, and clean formation of the phosphine derivative **12**. The same product was obtained by reaction of **11** with PMe_3. NMR spectra were consistent with the proposed structure, which was also confirmed by a single crystal X-ray diffraction study, discussed further below.

A similar reaction using perfluoro-n-propyl iodide yielded complex **13**, from which the CO analogue **14** and the PMe_3 derivative **15** could be prepared; complex **15** was also characterized by X-ray crystallography (see below). Similarly, treatment of the iridium analogue $TpIr(C_2H_4)_2$ with perfluoropropyl iodide afforded the ethylene complex **16**. However, treatment of this compound with PMe_3 did not result in displacement of ethylene, as observed with the rhodium analogue, but instead substitution of iodide occurred to give the salt **17** which was inert to loss of ethylene. This is not unprecedented, as reaction of $[TpIr(C_2H_4)_2I]I$ with PPh_3 is reported to produce a salt, $[TpIr(PPh_3)(C_2H_4)I]I$, from which the ethylene is not easily displaced.[29] Interestingly, the ethylene ligand in **17** exhibits four resonances in the ^1H NMR spectrum, consistent with slow propeller rotation on the NMR timescale, whereas that in **16** shows fast ethylene rotation down to −60 °C.

The relative electron-donating abilities of Tp and Cp ligands have been analyzed, based on their effect on the CO stretching frequencies of a series of carbonyl complexes.[30a] The conclusion for rhodium and iridium compounds was that the relative ordering was Cp* > Cp ≈ Tp* > Tp. The compounds prepared here allow comparison of a more extensive series. The CO stretching frequencies data for the complexes in this study and, where available, the corresponding Cp and Cp* complexes, are presented in Table 1. This series shows the same trend, and for both iridium and rhodium the ordering of θ_{CO} is consistent with the relative electron donating ability being Cp* > Cp > Tp* > Tp. Curiously, the ordering of Cp > Tp is the reverse of that suggested for complexes of Mo, on the basis of calculations.[30b]

Table 1 Carbonyl stretching frequencies for Cp*, Cp, Tp* and Tp fluoroalkyl complexes

Complex	ν_{CO} (CH_2Cl_2)
$Cp^*Rh(CF_2CF_2CF_3)CO(I)$ [40]	2069
$CpRh(CF_2CF_2CF_3)CO(I)$ [41]	2084
$Tp^*Rh(CF_2CF_2CF_3)CO(I)$ **6**	2103
$TpRh(CF_2CF_2CF_3)CO(I)$ **14**	2111
$Cp^*Ir(CF_2CF_2CF_3)CO(I)$ [3]	2045
$CpIr(CF_2CF_2CF_3)CO(I)$ [42]	2061
$TpIr(CF_2CF_2CF_3)CO(I)$ **4**	2084
$Cp^*Rh(CF_2C_6F_5)CO(I)$ [40]	2056
$Tp^*Rh(CF_2C_6F_5)CO(I)$ **5**	2098
$TpRh(CF_2C_6F_5)CO(I)$ **11**	2113
$Cp^*Ir(CF_2C_6F_5)CO(I)$ [3]	2039
$TpIr(CF_2C_6F_5)CO(I)$ **3**	2085

Crystallographic studies

Details of the crystallographic determinations and the solution refinements for **3**, **12**, and **15** are shown in Table 3. ORTEP drawings and labeling schemes are provided in Figs. 1–3, for **3**, **12**, and **15** respectively. Selected bond distances and angles are presented in Table 2. Compound **15** contains two independent molecules in the asymmetric unit. The solid state structures all show an approximate octahedral geometry as shown by interligand angles close to 90° (entries 8–19). The familiar [1,3,31,32] acute angle for F(11)–C(1)–F(12) (entry 20) along with an obtuse C(2)–C(1)–M angle (entry 21), is observed in all three cases. Comparison of M–N distances for compounds **12** and **15** (entries 4–6) indicates that the order of structural *trans*-influence is fluoroalkyl > PMe_3 > I. An analogous comparison of compounds **3** and **12** illustrates the poor *trans*-influence of CO.[31,33–37]

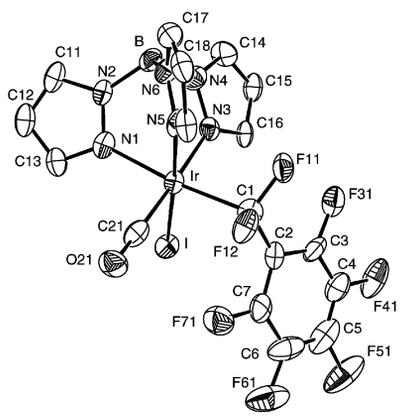


Fig. 1 ORTEP drawing of **3** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

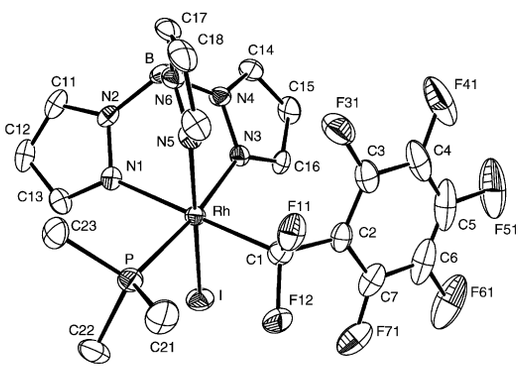


Fig. 2 ORTEP drawing of **12** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

Table 2 Selected bond lengths and angles of the crystallographically studied complexes. The atom labeling schemes are shown in Figs. 1–3

Entry	Length/angle	**3**	**12**	**15**[c]
1	M–C(1)	2.147(14)	2.063(5)	2.052(9), 2.078(10)
2	M–L	1.899(19)[a]	2.3006(14)[b]	2.295(2)[b], 2.301(2)[b]
3	M–I	2.6719(11)	2.6478(7)	2.6454(9), 2.6509(10)
4	M–N(1)	2.133(11)	2.166(4)	2.153(7), 2.154(7)
5	M–N(3)	2.075(11)	2.140(4)	2.138(7), 2.113(7)
6	M–N(5)	2.116(12)	2.084(4)	2.099(7), 2.074(7)
7	CNT[d]–M	1.291(11)	1.311(5)	1.314(7), 1.297(5)
8	C(1)–M–L	90.4(6)[a]	91.27(14)[b]	88.4(3)[b], 95.2(2)[b]
9	N(3)–M–C(1)	92.4(5)	95.80(17)	96.8(3), 91.2(3)
10	N(5)–M–C(1)	88.2(5)	93.52(18)	89.3(3), 86.3(3)
11	N(3)–M–N(5)	88.6(4)	88.24(14)	87.6(3), 88.1(3)
12	N(3)–M–N(1)	83.9(4)	83.30(14)	81.3(3), 83.1(3)
13	N(5)–M–N(1)	86.7(4)	86.77(15)	89.0(3), 87.7(3)
14	L–M–I	88.7(5)[a]	94.16(4)[b]	87.49(7)[b], 92.21(7)[b]
15	N(3)–M–I	90.0(3)	87.28(10)	90.06(19), 88.1(2)
16	N(1)–M–I	89.5(3)	89.93(10)	88.59(18), 89.3(2)
17	C(1)–M–I	95.6(4)	89.71(15)	93.0(2), 96.4(3)
18	L–M–N(1)	93.4(5)[a]	89.63(10)[b]	93.44(19)[b], 90.4(2)[b]
19	L–M–N(5)	92.4(6)[a]	89.94(11)[b]	94.7(2)[b], 91.3(2)[b]
20	F(11)–C(1)–F(12)	103.1(10)	101.7(4)	102.7(6), 101.7(7)
21	C(2)–C(1)–M	120.9(10)	118.6(3)	119.8(6), 126.0(6)
22	CNT[d]–M–C(1)	123.51(5)	129.63(10)	127.17(6), 121.69(10)
23	CNT[d]–M–I	122.68(5)	120.06(10	121.26(6), 120.39(10)
24	CNT[d]–M–L	126.21(5)[a]	122.39(10)[b]	128.02(6)[b], 123.75(10)[b]

[a] L = CO. [b] L = PMe_3. [c] Two independent molecules in asymmetric unit; the first value corresponds to molecule A and the second to molecule B, as defined in Fig. 3. [d] CNT is the centroid of N(1), N(2), and N(3).

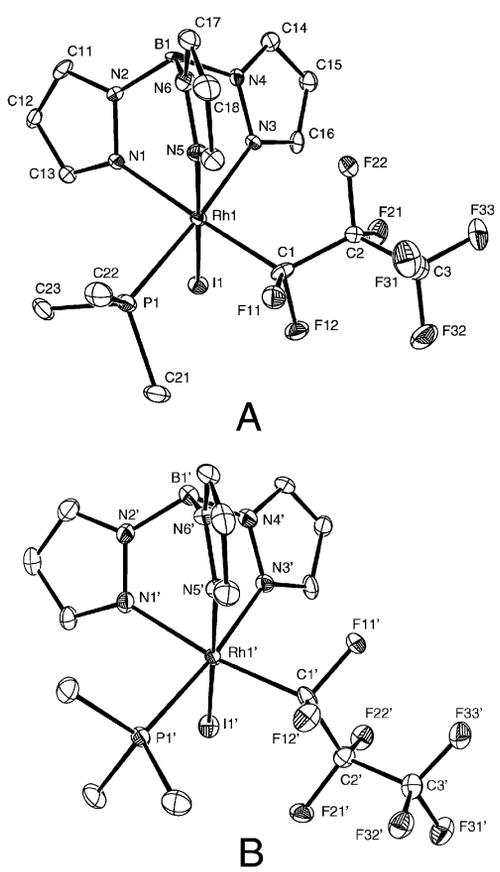


Fig. 3 ORTEP drawing of two independent molecules (A and B) of **15** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

We have chosen to compare the angles between the centroids of N(1)–N(3)–N(5) and the other ligands (entries 22–24). Centroids are commonly used in Cp and Cp* complexes to provide a common basis to define metal-ring distances and angles between other ligands. Before dealing with the centroid distances and angles, a brief comparison of individual parameters within the three complexes described here provides some initial benchmarks, particularly in regard to the conformational preferences of the fluorinated ligands with respect to their neighbors. In compound **3** (Fig. 4a) the perfluorobenzyl ligand adopts a conformation with the aryl ring canted away from the Tp ligand, such that the C(1)–C(2) bond is eclipsing the Ir–I bond, with a torsion angle I–Ir–C(1)–C(2) of 1.8°. The identical conformation of the perfluorobenzyl ligand is found in the structures of $Cp^*Ir(CF_2C_6F_5)(PMe_3)I$[3,38] and $Cp^*Rh(CF_2C_6F_5)(PPhMe_2)I$.[5] In contrast the same ligand in complex **12** adopts a conformation with the aryl ring tilted towards the Tp ligand such that the C(1)–C(2) bond is close to eclipsing the Rh–N(3), with the torsion angle N(3)–Rh–C(1)–C(2) being 11.1°. At first sight, this conformational change might be thought to be the result of an increased steric interaction between the fluorobenzyl ligand and the PMe_3 ligand in **12** compared to CO in **3**. However, examination of the two independent molecules in the asymmetric unit of the perfluoro-n-propyl complex **15** shows that molecule 1 adopts conformation (A) similar to that in **12**, with the perfluoropropyl ligand oriented towards the Tp ligand (Fig. 5a), with the torsion angle N(3)–Rh–C(1)–C(2) of 19.4°, whereas the second molecule (Fig. 5b) adopts a conformation (B) similar to that in **3**, with I(1)′–Rh′–C(1)′–C(2)′ being 7.3°. Accordingly, it seems that both conformations have similar energies, at least in the solid state, and that steric interactions with PMe_3 are not the cause of any conformational preferences. The conformational changes of the perfluoropropyl ligand in **15** are accompanied by some other significant changes as the molecule flexes to accommodate them. The changes in N–M–N angles (entries 11–13) are not dramatic, as expected due to the constrained geometry of Tp ligand. However, the fluoroalkyl ligand appears to have significant flexibility with regard to the angle at the α-carbon, with the change from conformation (A) to conformation (B) resulting in a significant opening up of the M–C(1)–C(2) angle (entry 21) from 119.8(6) to 126.0(6)°; interestingly this is not accompanied by any significant change in the F(11)–C(1)–F(12) angle (entry 20). The same conformational change results in significant contraction of the N(3)–M–C(1) angle from 96.8(3) to 91.2(2)° (entry 9), and significant opening of the C(1)–M–P

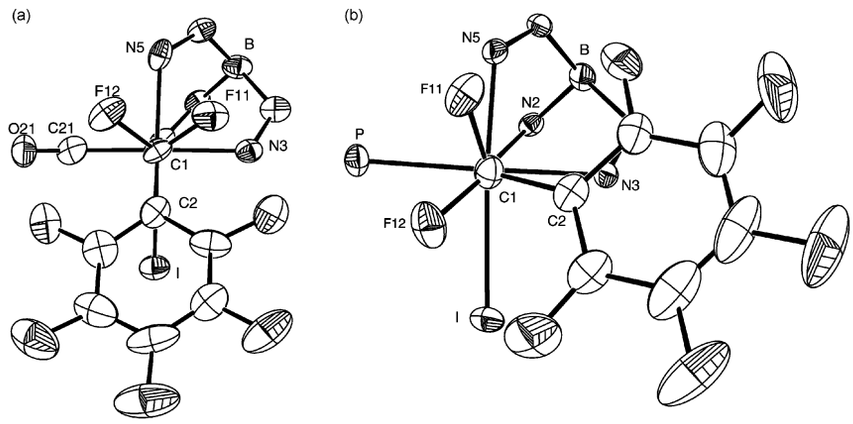


Fig. 4 ORTEP drawings of **3** (a) and **12** (b) viewed down the C(1)–M bond, with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms and carbon atoms of the pyrazole rings are omitted for clarity.

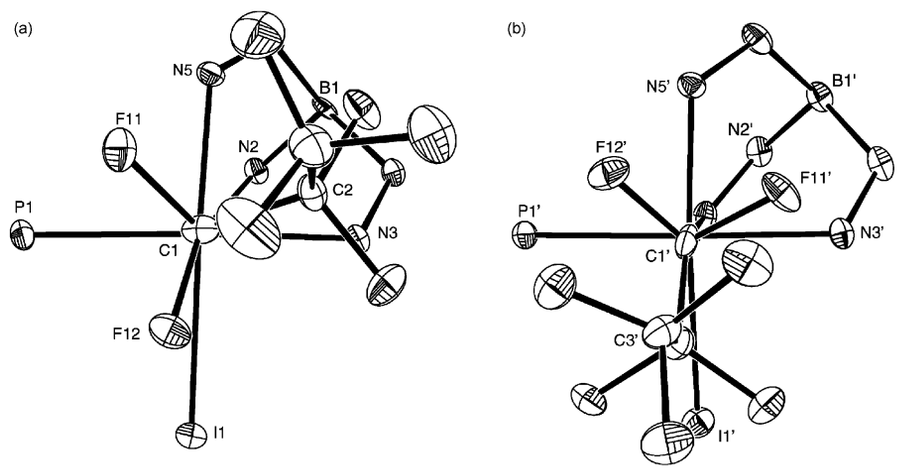


Fig. 5 ORTEP drawings of both independent molecules of **15** viewed down the C(1)–Rh bond, with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms and carbon atoms of the pyrazole rings are omitted for clarity.

and P–M–I angles (entries 8 and 14) from 88.4(3) to 95.2(2)°, and from 87.49(7) to 92.21(7)° respectively.

While the individual N–M–N angles do not change significantly as a result of conformational changes in the fluorinated ligand, comparison of angles between the N–N–N centroid and the other ligands in **15** (entries 22–24) reveals that the Tp ligand as a whole is indeed affected. When the perfluoropropyl ligand is in conformation (A) the CNT–M–C(1) angle is 127(17(6)° while in conformation (B) this contracts to 121.69(10)°. A similar contraction of CNT–M–P from 128.02(6) to 123.75(10)° is also observed, while the CNT–M–I angle remains virtually unaffected. Consequently, it seems that the flexing of the molecule to accommodate conformational change in the fluorinated ligand occurs by adjustment of the Tp and PMe_3 ligands rather than the iodide. Similar changes are observed resulting from the two different conformations of the perfluorobenzyl ligand in complexes **3** and **12**.

Experimental

All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which has been deoxygenated over BASF catalyst and dried over Aquasorb®, or in a Braun Drybox. Methylene chloride, hexane, diethyl ether and toluene were dried over an alumina column under nitrogen. IR spectra were recorded on a Perkin–Elmer FTIR 1600 Series spectrometer. NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometer. ^{1}H NMR spectra were referenced to the protio impurity in the solvent; C_6D_6 (δ 7.16), $CDCl_3$ (δ 7.27), CD_2Cl_2 (δ 5.32). ^{19}F NMR spectra were referenced to $CFCl_3$ (δ 0.00) and ^{31}P{^{1}H} NMR spectra were referenced to 85% H_3PO_4 (δ 0.00). $ICF_2CF_2CF_3$ (Lancaster) and $ICF_2C_6F_5$ (PCR) were washed with sodium thiosulfate to remove residual iodine, then vacuum distilled and deoxygenated by several cycles of freeze–pump–thaw. Carbon monoxide and ethylene were purchased from Matheson.

$TpIr(CH_2{=}CH_2)_2$,[22,25] $TpIr(CO)_2$,[22] $Tp^*Ir(CH_2{=}CH_2)_2$,[21] $TpRh(CH_2{=}CH_2)$,[24] $Tp^*Rh(CO)_2$,[20] and $Tp^*Rh(CH_2{=}CH_2)_2$[20] were prepared by literature methods. $Tp^*Ir(CO)_2$ was synthesized from $Tp^*Ir(CH_2{=}CH_2)_2$ (prepared in situ)[21] by treatment with excess CO and following the reaction by IR until it was complete. The solvent was removed in *vacuo* and the yellow residue was redissolved in toluene and filtered through Celite. The final product was isolated by removal of solvent (63%).

Synthesis

$TpIr(CF_2C_6F_5)I(CO)$ (3). $TpIr(C_2H_4)_2$ (200 mg, 0.434 mmol) was dissolved in benzene (20 mL) and CO was bubbled through the solution for 5 min to form $TpIr(CO)_2$ (ν_{CO} 2074, 1947, 1998 (br)). Perfluorobenzyl iodide (164 mg, 0.477 mmol) was added to the pale yellow benzene solution. The reaction mixture become orange and CO was evolved, after 1 h IR showed that no starting material remained. The solvent was removed *in vacuo* to give an orange–yellow powder. The product was purified by column chromatography (silica gel, 25 cm × 1.5 cm, −40 °C). A yellow band eluted with ether/hexanes (1 : 2) and was further purified by recrystallization from methanol and hexanes at −20 °C to give pale yellow crystals. Yield 216 mg (64%). IR (CH_2Cl_2): θ_{CO} = 2085 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.25 (d, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 8.18 (br, s, $1H_{3\ or\ 5}$), 8.05 (d, J_{HH} = 2.0, $1H_{3\ or\ 5}$), 7.80 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.72 (d, J_{HH} = 2.2, $1H_{3\ or\ 5}$),

7.68 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 6.41 (t, J_{HH} = 2.4, $1H_4$), 6.35 (t, J_{HH} = 2.4, $1H_4$), 6.30 (t, J_{HH} = 2.3, $1H_4$). ^{19}F NMR ($CDCl_3$): δ −46.6 (dt, J_{AB} = 258, J_{FF} = 20, 1F, $C_\alpha F_A$), −68.8 (dt, J_{AB} = 258, J_{FF} = 31, 1F, $C_\alpha F_B$), −139.0 (br, s, 2F, *ortho*), −155.4 (t, J_{FF} = 20, 1F, *para*), −163.0 (m, 2F, *meta*). ^{1}H NMR (acetone-d_6, −44 °C): δ 8.36 (d, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 8.22 (d, J_{HH} = 2.4, $2H_{3\ or\ 5}$), 8.17 (d, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 8.12 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 8.10 (br, s, $1H_{3\ or\ 5}$), 8.06 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 6.59 (t, J_{HH} = 2.4, $1H_4$), 6.52 (t, J_{HH} = 2.4, $1H_4$), 6.44 (t, J_{HH} = 2.2, $1H_4$); ^{19}F (acetone-d_6, −44 °C): δ −44.0 (dt, J_{AB} = 258, J_{FF} = 21, 1F, $C_\alpha F_A$), −67.5 (dt, J_{AB} = 258, J_{FF} = 35, 1F, $C_\alpha F_B$), −135.3 (br, s, 1F, *ortho*), −142.6 (br, s, 1F, *ortho*), −155.3 (t, J_{FF} = 21, 1F, *para*), −162.8 (br, s, 2F, *meta*). Anal. calc. for $C_{17}H_{10}BF_7IN_6OIr$ (777.2): C, 26.27; H, 1.30; N, 10.81. Found: C, 26.39; H, 1.25; N, 10.99.

TpIr($CF_2CF_2CF_3$)I(CO) (4). A THF solution (5 mL) of perfluoro-n-propyl iodide (77 mg, 0.26 mmol) was added to a yellow THF solution (10 mL) of $TpIr(CO)_2$ (120 mg, 0.26 mmol.). The reaction mixture become orange/yellow and CO was evolved. After 1 h, no starting material remained by IR, and the solvent was removed *in vacuo* to give an orange–yellow powder, 106 mg (58%). IR (CH_2Cl_2): θ_{CO} = 2084 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.50 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 8.18 (d, J_{HH} = 2.1, $1H_{3\ or\ 5}$), 7.84 (d, J_{HH} = 2.4, $2H_{3\ or\ 5}$), 7.82 (dd, J_{HH} = 2.4, J_{HF} = 0.5, $1H_{3\ or\ 5}$), 7.78 (dd, J_{HH} = 2.5, J_{HF} = 0.5, $1H_{3\ or\ 5}$), 6.44 (t, J_{HH} = 2.4, $1H_4$), 6.40 (t, J_{HH} = 2.4, $1H_4$), 6.38 (t, J_{HH} = 2.1, $1H_4$). ^{19}F NMR (CD_2Cl_2): −77.9 (ddqd, J_{AB} = 273, $^3J_{FF}$ = 7.3, $^3J_{FF}$ = 8.1, $^4J_{FF}$ = 12.4, 1F, $C_\alpha F_A$), −78.9 (t, J_{FF} = 12.4, CF_3), −88.3 (ddqd, J_{AB} = 273, $^3J_{FF}$ = 8.1, $^3J_{FF}$ = 11.3, $^4J_{FF}$ = 12.4, 1F, $C_\alpha F_B$) −113.5 (ddd, J_{AB} = 285, $^3J_{FF}$ = 7.3, $^3J_{FF}$ = 11.3, 1F, $C_\beta F_A$), −117.0 (dt, J_{AB} = 285, $^3J_{FF}$ = 8.1, 1F, $C_\beta F_B$). Anal. calc. for $C_{13}H_{10}BF_7IN_6OIr$ (729.19): C, 21.41; H, 1.38. Found: C, 21.75; H, 1.54.

Tp*Rh($CF_2C_6F_5$)I(CO) (5). Tp*Rh(CO)$_2$ (55 mg, 0.121 mmol) was suspended in benzene (10 mL) and perfluorobenzyl iodide (50 mg, 0.146 mmol) was added. The solution color changed from yellow to orange–yellow. After 5 h, the volatiles were removed. The product was purified by chromatography (silica gel, 1.5 cm × 12 cm), eluting with hexanes. Yield 45% (42 mg). IR (CH_2Cl_2): θ_{CO} = 2098 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.91 (s, 1H), 5.89 (s, 1H), 5.76 (s, 1H), 2.60 (s, 3H), 2.44 (s, 6H), 2.42 (s, 6H), 2.31 (s, 3H). ^{19}F NMR ($CDCl_3$): δ −28.05 (d, J_{AB} = 219, 1F, $C_\alpha F_A$), −54.1 (dt, J_{AB} = 219, J_{FF} = 39, 1F, $C_\alpha F_B$), −134.4 (m, 2F, *ortho*), −153.9 (m, 1F, *para*), −162.9 (m, 2F, *meta*). Anal. calc. for $C_{23}H_{22}BF_7IN_6ORh$ (772.1): C, 35.78; H, 2.87. Found: C, 35.77; H, 2.81.

Tp*Rh($CF_2CF_2CF_3$)I(CO) (6). A THF solution (5 mL) of perfluoropropyl iodide (71 mg, 0.24 mmol) was added to a yellow THF (10 mL) solution of Tp*Rh(CO)$_2$ (110 mg, 0.24 mmol.) The reaction mixture become red and CO was evolved. After 1 h, no starting material remained by IR, and the solvent was removed *in vacuo* to give a red powder 148 mg (85%). IR (CH_2Cl_2): θ_{CO} = 2103 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 6.04 (s, 1H), 5.97 (s, 1H), 5.86 (s, 1H), 2.67 (s, 3H), 2.65 (s, 3H), 2.51 (s, 3H), 2.46 (s, 3H), 2.97 (s, 3H), 2.38 (s, 3H). ^{19}F NMR (CD_2Cl_2): δ −54.4 (dbr, J_{AB} = 261, 1F, $C_\alpha F_A$), −58.8 (dbr, J_{AB} = 261, 1F, $C_\alpha F_B$), −80.3 (dd, J_{FF} = J_{FF} = 12, CF_3), −116.3 (dbr, J_{AB} = 286, 1F, $C_\beta F_A$), −117.9 (dd, J_{AB} = 286, J_{FF} = 12.4, 1F, $C_\beta F_B$). Anal. calc. for $C_{19}H_{22}BF_7IN_6ORh$ (724.02): C, 31.52; H, 3.06. Found: C, 31.17; H, 2.94.

TpRh($CF_2C_6F_5$)I(C_2H_4) (7). TpRh(C_2H_4)$_2$ (200 mg, 0.538 mmol) was dissolved in THF (8 mL) and the yellow solution cooled to −70 °C. A solution of perfluorobenzyl iodide (185 mg, 0.538 mmol) in THF (2 mL) was added to the reaction mixture. The mixture was warmed from −70 to −10 °C over 8 h, and then to room temperature. The product was isolated by precipitation with hexanes to give a burnt orange powder. Yield 15% (54 mg). ^{1}H NMR (C_6D_6): δ 8.05 (d, J_{HH} = 2.0, $1H_{3\ or\ 5}$), 7.90 (br, s, $1H_{3\ or\ 5}$), 7.77 (d, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 7.28 (d, J_{HH} = 2.5, $1H_{3\ or\ 5}$), 7.27 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.05 (d, J_{HH} = 2.5, $1H_{3\ or\ 5}$), 5.91 (t, J_{HH} = 2.1, $1H_4$), 5.91 (t, J_{HH} = 2.1, $1H_4$), 5.85 (t, J_{HH} = 2.3, $1H_4$), 5.57 (t, J_{HH} = 2.3, $1H_4$), 2.33 (br, s, 2H, C_2H_4), 0.75 (br, s, 2H, C_2H_4). ^{19}F NMR (C_6D_6): δ −66.2 (m, 2F, CF_2), −138.7 (br, s, 2F, *ortho*), −156.0 (t, J_{FF} = 23, 1F, *para*), −163.0 (m, 2F, *meta*). ^{19}F NMR (diethylether): δ −64.4 (dt, J_{AB} = 229, J_{FF} = 25, 1F, $C_\alpha F_A$), −65.4 (dt, J_{AB} = 229, J_{FF} = 31, 1F, $C_\alpha F_B$), −138.2 (br, s, 2F, *ortho*), −157.3 (t, J_{FF} = 23, 1F, *para*), −163.9 (m, 2F, *meta*). Satisfactory microanalysis could not be obtained on this compound, but was obtained for its CO and PMe_3 derivatives **11** and **12** (below).

TpRh($CF_2C_6F_5$)I(CO) (11). TpRh($CF_2C_6F_5$)I(C_2H_4) (**7**) (129 mg, 0.187 mmol) was dissolved in benzene (10 mL) and CO was bubbled through the orange solution for 30 min. The reaction was stirred overnight and volatiles were removed *in vacuo* to leave a burnt orange powder, which was recrystallized from CH_2Cl_2/MeOH. Yield 45% (42 mg). IR (CH_2Cl_2): θ_{CO} = 2113 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.20 (d, J_{HH} = 2.0, $1H_{3\ or\ 5}$), 8.09 (d, J_{HH} = 2.4, $2H_{3\ or\ 5}$), 8.03 (d, J_{HH} = 2.0, $1H_{3\ or\ 5}$), 7.98 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.90 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 6.52 (t, J_{HH} = 2.5, $1H_4$), 6.42 (t, J_{HH} = 2.5, $1H_4$), 6.33 (t, J_{HH} = 2.3, $1H_4$). ^{19}F NMR (acetone-d_6): δ −38.4 (dt, J_{AB} = 219, J_{FF} = 23, 1F, $C_\alpha F_A$), −58.7 (dt, J_{AB} = 219, J_{FF} = 31, 1F, $C_\alpha F_B$), −137.8 (br, s, 2F, *ortho*), −154.9 (t, J_{FF} = 23, 1F, *para*), −163.0 (m, 2F, *meta*). Anal. calc. for $C_{17}H_{10}BF_7IN_6ORh$ (687.9): C, 29.68; H, 1.47; N, 12.22. Found: C, 29.77; H, 1.48; N, 12.03.

TpRh($CF_2C_6F_5$)I(PMe_3) (12). Compound **7** was generated *in situ* (0.538 mmol) and PMe_3 (56 μL, 0.538 mmol) added. The solution was stirred for 24 h, filtered and the solvent was removed. The residue was redissolved in CH_2Cl_2, methanol was layered on the solution and at −60 °C yellow crystals formed. Yield 30% (118 mg). Alternatively, a solution of compound **11** in C_6D_6 was treated with excess PMe_3, resulting in the formation of the same product. ^{1}H ($CDCl_3$): δ 8.05 (br, $1H_{3\ or\ 5}$), 7.99 (d, J_{HH} = 2.2, $2H_{3\ or\ 5}$), 7.82 (d, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 7.63 (d, J_{HH} = 2.2 $1H_{3\ or\ 5}$), 7.57 (br, m, $1H_{3\ or\ 5}$), 6.99 (br, s, $1H_{3\ or\ 5}$), 6.33 (t, J_{HH} = 2.3, $1H_4$), 6.19 (t, J_{HH} = 2.0, $1H_4$), 5.95 (dt, J_{HH} = 1.7, $J_{HRh\ or\ B}$ = 2.1 $1H_4$), 1.69 (d, J_{HP} = 11.0, PMe_3). ^{19}F NMR ($CDCl_3$): δ −26.0 (ddtd, J_{AB} = 227, J_{FRh} = 10, J_{FF} = 36, J_{FP} = 37, 1F, $C_\alpha F_A$), −41.7 (dm, J_{AB} = 227, $C_\alpha F_B$), −138.4 (br, s, 2F, *ortho*), −156.5 (t, J_{FF} = 21, 1F, *para*), −163.8 (br, s, 2F, *meta*); ^{31}P{^{1}H} ($CDCl_3$) δ 7.7 (ddd, J_{PRh} = 123, J_{PFb} = 40, J_{PFa} = 12, PMe_3). ^{1}H NMR (acetone-d_6, −44 °C): δ 8.19 (br, t, $1H_{3\ or\ 5}$), 8.08 (d, J_{HH} = 2.2, $2H_{3\ or\ 5}$), 7.89 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.81 (br, m, $1H_{3\ or\ 5}$), 6.87 (d, J_{HH} = 2.0, $1H_{3\ or\ 5}$), 6.45 (br, s, $1H_{3\ or\ 5}$), 6.35 (t, J_{HH} = 2.3, $1H_4$), 6.27 (t, J_{HH} = 2.2, $1H_4$), 6.03 (dt, J_{HH} = 2.2, $J_{HRh\ or\ B}$ = 1.5 $1H_4$), 1.69 (d, J_{HP} = 11.4, PMe_3). ^{19}F NMR (acetone-d_6, −44 °C): δ −41.5 (dddd, J_{AB} = 228,J_{FRh} = 10, J_{FF} = 17, J_{FP} = 41, 1F, $C_\alpha F_A$), −41.7 (dm, J_{AB} = 228, $C_\alpha F_B$), −137.3 (dd, J_{FF} = 73, J_{FP} = 23, 1F, *ortho*), −138.4 (t, J_{FF} = 25, 1F, *ortho*) −156.2 (t, J_{FF} = 22, 1F, *para*), −162.6 (t, J_{FF} = 22, 1F, *meta*), −165.6 (t, J_{FF} = 22, 1F, *meta*); ^{31}P{^{1}H} (acetone-d_6, −44 °C) δ 11.4 (ddd, J_{PRh} = 121, J_{PFb} = 40, J_{PFa} = 11, PMe_3). Anal. calc. for $C_{19}H_{19}BF_7IN_6PRh$ (736.0): C, 31.02; H, 2.60; N, 11.42. Found: C, 30.87; H, 2.33; N, 11.27.

TpRh($CF_2CF_2CF_3$)(C_2H_4)I (13). An ether solution of perfluoropropyl iodide (80 mg, 0.27 mmol) was added to a yellow THF solution of TpRh(C_2H_4)$_2$ (100 mg, 0.27 mmol). The reaction mixture become yellow/orange and C_2H_4 was evolved. The solution was filtered through celite and the solvent removed *in vacuo*. The residue was extracted with ether and then hexanes added. Filtration followed by removal of hexanes

yielded a yellow/orange powder, 95 mg (32%). ^{1}H NMR (C_6D_6): 8.63 (br, $1H_{3\ or\ 5}$), 8.45 (d, J_{HH} = 2, $1H_{3\ or\ 5}$), 8.13 (d, J_{HH} = 2, $1H_{3\ or\ 5}$), 7.89 (br, $1H_{3\ or\ 5}$), 7.32 (br, $2H_{3\ or\ 5}$), 5.95 (t, J = 2, $2H_4$), 5.66 (t, J = 2, $1H_4$), 1.85 (br, 2H, CH_2=CH_2), 1.64 (br, 2H, CH_2=CH_2). ^{19}F NMR (CD_2Cl_2): δ −77.8 (dm, J_{AB} = 255, 1F, $C_\alpha F_A$), −82.7 (dbr, J_{AB} = 255, 1F, $C_\alpha F_B$), −79.8 (t, J_{FF} = 12.4, CF_3), −116.8 (ddd, J_{AB} = 289, $^3J_{FF}$ = 16.1, $^3J_{FF}$ = 5.1, 1F, $C_\beta F_A$), −128.3 (ddd, J_{AB} = 289, $^3J_{FF}$ = 13.1, $^3J_{FF}$ = 8.8, 1F, $C_\beta F_B$).

TpRh($CF_2CF_2CF_3$)I(CO) (14). A CH_2Cl_2 (10 mL) solution of **13** was saturated with CO. The reaction was monitored by ^{19}F NMR, and was complete after several days under a CO atmosphere. IR (CH_2Cl_2): θ_{CO} = 2111 cm^{-1}; ^{19}F (CD_2Cl_2): δ −78.8 (dbr, J_{AB} = 303, 1F, $C_\alpha F_A$), −76.0 (dbr, J_{AB} = 243, 1F, $C_\alpha F_B$), −79.8 (t, J_{FF} = 12.3, CF_3), −116.9 (J_{AB} = 289, J = 14.4, J = 8.0 1F, $C_\beta F_A$), −120.3 (J_{AB} = 289, J = 16.2, J = 4.2, 1F, $C_\beta F_B$).

TpRh($CF_2CF_2CF_3$)I(PMe_3) (15). An ether solution of trimethylphosphine (12 mg, 0.16 mmol) was added to a yellow/orange ether (10 mL) solution of **13** (100 mg, 0.16 mmol). The reaction mixture darkened and C_2H_4 was evolved. The solution was filtered through celite and the solvent was removed *in vacuo* to give a yellow/orange powder, 68 mg (62%). Crystals suitable for X-ray analysis were grown from CH_2Cl_2/MeOH. ^{1}H NMR (CD_2Cl_2): δ 8.27 (t, J_{HH} = 2.1, $1H_{3\ or\ 5}$), 8.18 (d, J_{HH} = 2.1, $1H_{3\ or\ 5}$), 7.94 (d, J_{HH} = 2.4 $1H_{3\ or\ 5}$), 7.90 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.76 (dd, J_{HRh} = 0.5, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 7.56 (m, J_{HP} = 1.8 J_{HRh} = 1.5, J_{HH} = 2.5, $1H_{3\ or\ 5}$), 6.39 (t, J_{HH} = 2.4, $1H_4$), 6.19 (t, J_{HH} = 2.4, $1H_4$), 6.16 (dt, J_{PH} = 1.8 J_{HH} = 2.2, $1H_4$) 1.73 (d, J_{HH} = 11.4 PMe_3); ^{1}H{^{31}P} NMR (CD_2Cl_2): δ 8.27 (t, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 8.18 (d, J_{HH} = 2.1, $1H_{3\ or\ 5}$), 7.94 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.90 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.76 (dd, J_{HRh} = 0.5, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 7.69 (dd, J_{RhH} = 0.5, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 6.39 (t, J_{HH} = 2.4, $1H_4$), 6.27 (t, J_{HH} = 2.2, $1H_4$), 6.23 (t, J_{HH} = 2.2, $1H_4$) 1.73 (s, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −66.3 (dm, J_{AB} = 268, 1F, $C_\alpha F_A$), −74.02 (dbr, J_{AB} = 268, 1F, $C_\alpha F_B$), −79.5 (t, J_{FF} = 12.4, CF_3), −114.4 (dt, J_{AB} = 286, J_{FF} = 8.2, 1F, $C_\beta F_A$), −117.6 (dd, J_{AB} = 286, J_{FF} = 12.4, 1F, $C_\beta F_B$); ^{31}P{^{1}H} (CD_2Cl_2) 3.52 (dt, J_{RhP} = 117, $^3J_{PF}$ = 24). Anal. calc. for $C_{15}H_{19}BF_7IPN_6Rh$ (687.94): C, 26.19; H, 2.78. Found: C, 26.42; H, 3.03.

TpIr($CF_2CF_2CF_3$)I(C_2H_4) (16). A CH_2Cl_2 solution (5 mL) of perfluoropropyl iodide (77 mg, 0.26 mmol) was added to a yellow CH_2Cl_2 solution (10 mL) of Tp$Ir(C_2H_4)_2$ (120 mg, 0.26 mmol). The reaction mixture turned yellow/orange and C_2H_4 was evolved. The solution was filtered through celite and the solvent was removed *in vacuo* to give a yellow/orange powder, 127 mg (70%). ^{1}H NMR (CD_2Cl_2): δ 8.45 (br, 2.1, $1H_{3\ or\ 5}$), 7.94 (d, J_{HH} = 2.1, $H_{3\ or\ 5}$), 7.83 (d, J_{HH} = 2.1, $2H_{3\ or\ 5}$), 7.78 (dd, J_{HH} = 2.4, J_{HH} = 0.5, $H_{3\ or\ 5}$), 7.75 (dd, J_{HH} = 2.1, J_{HH} = 0.5, $1H_{3\ or\ 5}$), 6.41 (t, J_{HH} = 2.4, $1H_4$), 6.37 (t, J_{HH} = 2.1, $1H_4$), 6.35 (t, J_{HH} = 2.4, $1H_4$), 4.95 (m, 2H, CH_2=CH_2), 4.76 (m, 2H, CH_2=CH_2). ^{19}F NMR (CD_2Cl_2): δ −79.7 (t, $^4J_{FF}$ = 13.1), −82.7 (ddqd, J_{AB} = 288, $^3J_{FF}$ = 5.0, $^3J_{FF}$ = 12.1, $^4J_{FF}$ = 13.1, 1F, $C_\alpha F_A$), −85.2 (ddqd, J_{AB} = 288, $^3J_{FF}$ = 0.6, $^3J_{FF}$ = 10.8, $^4J_{FF}$ = 13.1, 1F, $C_\alpha F_B$), −116.5 (ddd, J_{AB} = 287, $^3J_{FF}$ = 5.0, $^3J_{FF}$ = 10.8, 1F, $C_\beta F_A$), −117.9 (ddd, J_{AB} = 287, $^3J_{FF}$ = 0.6, $^3J_{FF}$ = 12.1, 1F, $C_\beta F_B$). Anal. calc. for $C_{14}H_{14}BF_7IN_6Ir$ (729.23): C, 23.06; H, 1.94. Found: C, 23.34; H, 1.99.

[TpIr($CF_2CF_2CF_3$)(CH_2=CH_2)(PMe_3)]I (17). An ether solution (5 mL) of trimethylphosphine (11 mg, 0.14 mmol) was added to a yellow/orange ether solution (10 mL) of **16** (100 mg, 0.14 mmol). A precipitate was formed and the solution darkened. The solution was filtered to give a yellow/orange powder, 95 mg (86%). ^{1}H (CD_2Cl_2): 8.16 (t, J_{HH} = 2.2, $1H_{3\ or\ 5}$), 8.06 (d, J_{HH} = 2.1, $1H_{3\ or\ 5}$), 7.83 (d, J_{HH} = 2.1, $1H_{3\ or\ 5}$), 7.75 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.71 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 7.67 (d, J_{HH} = 2.4, $1H_{3\ or\ 5}$), 6.26 (t, J_{HH} = 2.4, $2H_4$), 6.24 (t, J_{HH} = 2.4, $1H_4$), 3.0 (m, 1H, CH_2=CH_2), 2.6 (m, 1H, CH_2=CH_2), 2.3 (m, 1H, CH_2=CH_2), 2 (m, 1H, CH_2=CH_2), 1.77 (d, J_{HH} = 13.2, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −77.4 (dm, J_{AB} = 288, $^3J_{FF}$ = 9.3, $^3J_{FF}$ = 13.3, $^4J_{FF}$ = 12.8, 1F, $C_\alpha F_A$), −84.4 (J_{AB} = 288, $^3J_{FF}$ = 9.3, $^4J_{FF}$ = 12.8, 1F, $C_\alpha F_B$), −79.6 (t, $^4J_{FF}$ = 12.8, CF_3), −116.5 (dt, J_{AB} = 285, $^3J_{FF}$ = 9.3, 1F, $C_\beta F_A$), −118.5 (J_{AB} = 285, $^3J_{FF}$ = 13.3, 1F, $C_\beta F_B$); ^{31}P{^{1}H} (CD_2Cl_2) 3.52 (dt, J_{RhP} = 117, $^3J_{PF}$ = 22.5). Anal. calc. for $C_{15}H_{19}BF_7IPN_6Ir$ (777.25): C, 23.18; H, 2.46. Found: C, 23.42; H, 2.57.

Crystallographic studies

Details of the crystal, data collection, and refinement parameters are provided in Table 3. The systematic absences in the diffraction data are uniquely consistent with the reported space groups. Complex **15** exists as two crystallographically independent molecules per asymmetric unit. The structures were solved by direct methods, completed by difference Fourier syntheses and refined by full-matrix least squares procedures. An empirical absorption correction was applied to the data of all compounds using the program DIFABS.[39] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. All software is contained in the SHELXTL program libraries (various versions, G. Sheldrick, Bruker AXS, Madison, WI).

CCDC reference numbers 186264–186266.

See http://www.rsc.org/suppdata/dt/b2/b202240k/ for crystallographic data in CIF or other electronic format.

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