Organometallic Reactivity Patterns in Fluorocarbons and Implications for Catalysis: Synthesis, Structure, Solubility, and Oxidative Additions of a Fluorous Analogue of Vaska's Complex, *trans*-$Ir(CO)(Cl)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$

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The reaction of $[Ir(Cl)(cod)]_2$, $P(CH_2CH_2(CF_2)_5CF_3)_3$, and CO (1 atm) gives the title compound (**2**, 97%). Tri(*n*-octyl)phosphine (**3**) and rhodium (**4**) analogues are similarly prepared. Crystal structures of **2** and **4** show anti CCCC conformations in the six perfluoroalkyl groups (average torsion angle 169°), with four chains (two per phosphorus) in parallel coplanar arrays that define ca. 21 × 6 Å "rafts". The other two chains extend on a common side of the raft, which pack back-to-back in stacks, maximizing parallel chains in every dimension. DSC shows one phase transition (melting, **2**/**4** 75/79 °C) prior to thermal decomposition (>200 °C). The IR ν_{CO} values (**2**/**3**/**4** 1975/1942/1979 cm^{-1}) show that the CH_2-CH_2 spacers do not completely insulate the metals from the perfluoroalkyl groups. Both **2** and **4** are soluble in $CF_3C_6F_{11}$, $CF_3C_6H_5$, ether, THF, and acetone but insoluble in hexane, toluene, $CHCl_3$, and CH_2Cl_2 ($CF_3C_6F_{11}$/THF partition coefficient >99.7:<0.3). Reactions of **2** with RI, H_2, and $^3O_2$ or $^1O_2$ in $CF_3C_6F_{11}$ give $Ir(CO)(Cl)(R)(I)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (R = $CH_2CH_2(CF_2)_7CF_3$ (**5**), CH_3 (**6**), $CH(CH_3)CH_2CH_3$ (**7**), 70−84%), $Ir(CO)(Cl)(H)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (82%), and $Ir(CO)(Cl)(O_2)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**9**, 67%), respectively. Additions of RI occur by free-radical chain mechanisms (inhibition by duroquinone; slower dark reactions; rates **7** > **5** > **6**) with no evidence for polar pathways. Complex **9** forms more rapidly in THF, indicating that (relative to THF) **2** and $^3O_2$ are stabilized by $CF_3C_6F_{11}$ more than the transition state.

Homogeneous transition metal catalysts are utilized in countless bench-scale and commodity chemical transformations.[2] However, critical needs remain for improved catalyst recovery methodologies and higher or new types of selectivities. In pursuit of these objectives, we have developed a conceptually new protocol—"fluorous biphase catalysis". As described in detail elsewhere,[3] this entails derivatizing catalysts with fluoroalkyl groups or "pony tails" of the formula $(CH_2)_y(CF_2)_xCF_3$ ($x \geq 5$). These appendages confer high solubilities in fluorous media, such as perfluoroalkanes, based upon the simple principle of "like dissolves like". Electronic properties can be "tuned" by varying the length of the $(CH_2)_y$ spacer. Many combinations of fluorous and organic solvents give bilayers, allowing facile separations of catalysts from products.

We have synthesized rhodium(I) catalysts that feature the previously reported fluorous phosphine $P(CH_2CH_2(CF_2)_5CF_3)_3$,[3a] effect a variety of transformations, can be extensively recycled, and possess many attractive attributes.[3−5] Novel fluorous catalysts or reagents are also being developed in other laboratories.[6] However, numerous fundamentally important underlying issues have yet to be addressed. For example, how are the structures of compounds with multiple pony tails best visualized? To what extent are electronic effects transmitted through $(CH_2)_y$ spacers? Can significant selectivity changes occur in fluorous solvents? How is the reactivity of oxygen, which is highly soluble in fluorous media, affected? Do the carbon−fluorine bonds introduce new deactivation pathways?[7]

For our initial investigation of these points, we sought to make use of the large body of structural, reactivity, and mechanistic data involving Vaska's complex, *trans*-

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[1] (a) University of Utah. (b) Exxon Research and Engineering.

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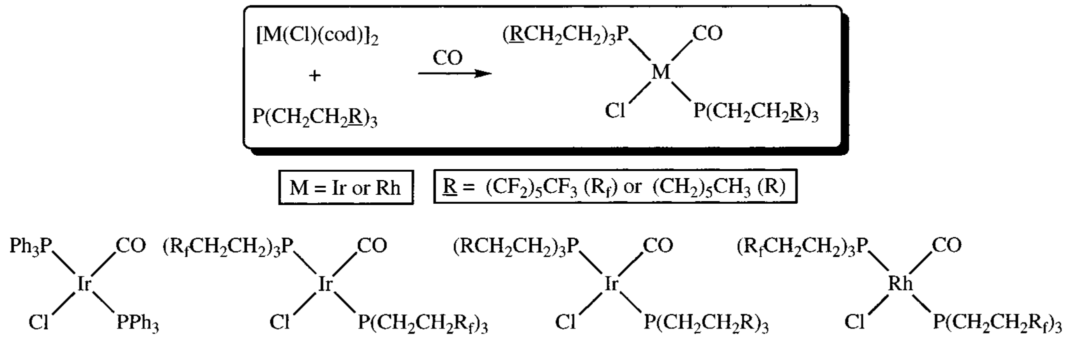
Scheme 1. Syntheses and IR and Solubility Properties of Iridium and Rhodium Complexes



	1	**2**	**3**	**4**
IR (ν_{CO}, Nujol)	1952 cm^{-1}	1975 cm^{-1}	1942 cm^{-1}	1979 cm^{-1}
$CF_3C_6F_{11}$	insol	sol	insol	sol
$CF_3C_6H_5$	insol	sol	sol	sol
pentane	insol	insol	sol	insol
hexane	insol	insol	sol	insol
ether	insol	sol	sol	sol
acetone	insol	sol	sol	sol
$CHCl_3$	sol	insol	sol	insol
CH_2Cl_2	sol	insol	sol	insol
THF	sol	sol	sol	sol
toluene	insol	insol	sol	insol

$Ir(CO)(Cl)(PPh_3)_2$ (**1**), and similar bis(phosphine) adducts.[8] We, therefore, turned our attention to the preparation of iridium(I) relatives of the rhodium(I) catalysts and the systematic study of the most common types of addition processes in homogeneous catalysis, as described below. Portions of this work have been communicated.[9]

Results

1. Syntheses of Iridium(I) Complexes. Complexes of the formula *trans*-$Ir(CO)(Cl)(PR_3)_2$ are easily prepared from $[Ir(Cl)(cod)]_2$ and the constituent ligands.[10] Thus, as shown in Scheme 1, $[Ir(Cl)(cod)]_2$ and $P(CH_2CH_2(CF_2)_5CF_3)_3$ were combined in hexane/CH_2Cl_2[10] under 1 atm of CO.[11] Workup gave *trans*-$Ir(CO)(Cl)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**2**) as an analytically pure, air-stable light yellow powder in 97% yield. Complex **2**, and all other new compounds below, were characterized by IR, ^1H NMR, and ^{31}P NMR spectroscopies, as summarized in the Experimental Section. However, ^{13}C NMR spectra were complicated by extensive ^{19}F couplings and were not generally recorded.

For comparison purposes, we sought analogues of **2** in which (a) all fluorines were replaced by hydrogens or (b) the iridium was replaced by rhodium. Accordingly, a similar reaction with commercially available tri(*n*-octyl)phosphine, $P((CH_2)_7CH_3)_3$, gave *trans*-$Ir(CO)(Cl)[P((CH_2)_7CH_3)_3]_2$ (**3**) as a yellow oil in 84% yield. Reaction of the rhodium precursor $[Rh(Cl)(cod)]_2$, the fluorous phosphine $P(CH_2CH_2(CF_2)_5CF_3)_3$, and CO gave *trans*-$Rh(CO)(Cl)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**4**) as an analytically pure light yellow powder in 98% yield.[12] The IR ν_{CO} values and solubility properties of **1**−**4** are summarized in Scheme 1. The former increase as the electron density on iridium decreases. Hence, the trend **2** > **3** shows that the phosphorus atoms and CH_2CH_2 spacers do not completely insulate the iridium from the electron-withdrawing perfluoroalkyl groups. The effect per pony tail is 5.5 cm^{-1}.

The solubility profiles of the fluorinated complexes **2** and **4** are identical and are instructive to compare with that of the rhodium(I) tris(phosphine) complex $Rh(Cl)[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$.[4] The last compound has nine pony tails and is very soluble in $CF_3C_6F_{11}$ and the partially fluorinated solvent $CF_3C_5H_6$[6c] but insoluble or very slightly soluble (acetone, THF) in common organic solvents. However, **2** and **4**, which have six pony tails, are soluble in ether, acetone, and THF, as well as $CF_3C_6F_{11}$ and $CF_3C_6H_5$. This shows that the solubilities of closely related compounds can be markedly affected by the number of pony tails. For the mechanistic goals of this study, the common solubility of **1**−**4** in THF is

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(10) Burk, M. J.; Crabtree, R. H. *Inorg. Chem.* **1986**, *25*, 931.

(11) Gas pressures are given in atmospheres according to the following convention: ambient = 1 atm; 15 and 30 psi gauge readings = 2 and 3 atm.

(12) (a) While this manuscript was in the final stages of preparation, an independent synthesis and crystal structure of **4** was reported, see: Fawcett, J.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Russell, D. R.; Stuart, A. M.; Cole-Hamilton, D. J.; Payne, M. J. *J. Chem. Soc., Chem. Commun.* **1997**, 1127. (b) The efforts appear to have been remarkably contemporaneous, as suggested by receipt dates of April 15, 1997[12a] and April 14, 1997 (our communication to the Cambridge Structural Database).

Table 1. Summary of Crystallographic Data for *trans*-Ir(CO)(Cl)[P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]$_2$ (2) and *trans*-Rh(CO)(Cl)[P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]$_2$ (4)

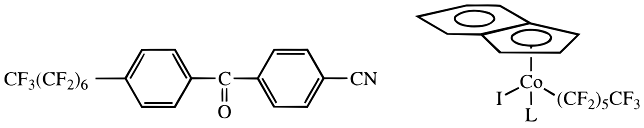
mol formula	$C_{49}H_{24}ClF_{78}IrOP_2$	$C_{49}H_{24}ClF_{78}OP_2Rh$
mol wt	2400.27	2310.98
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
temp. of collection (°C)	−80(2)	−80(2)
cell dimens		
a, Å	11.277(6)	11.256(3)
b, Å	15.094(5)	15.112(3)
c, Å	22.595(4)	22.553(6)
α, deg	84.83(2)	84.83(2)
β, deg	85.85(2)	85.93(3)
γ, deg	80.15(3)	80.25(2)
V, Å^3	3768(2)	3759(2)
Z	2	2
d_{calc}, g/cm^3	2.116	2.042
cryst dimens, mm	0.34 × 0.28 × 0.22	0.33 × 0.25 × 0.22
diffractometer	CAD4	CAD4
radiation (Å)	λ(Mo Kα) 0.710 73	λ(Mo Kα) 0.710 73
data collection method	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	variable	variable
no. of reflns meas	12 450	12 426
range/indices (h, k, l)	0 to 12; −17 to 17; −25 to 25	0 to 12; −17 to 17; −25 to 25
θ limit, deg	2.0−24.0	2.0−24.0
total no. of unique data	11 783	11 709
no. of obsd data, $I > 2\sigma(I)$	9781	8861
abs coeff, mm^{-1}	2.082	0.538
min transmission, %	83.6	97.0
max transmission, %	99.9	99.9
no. of variables	1262	1280
goodness of fit	1.050	1.037
$R1 = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|\ (2\sigma)$	0.046	0.0556
$wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$	0.1195	0.1515
R_{int}	0.0324	0.0263
R indices (all data)	R1 = 0.0637; wR2 = 0.1442	R1 = 0.0853; wR2 = 0.2584
Δ/σ (max)	0.000	0.002
Δ/ρ (max), e/Å^3	0.892	0.798
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2

advantageous, allowing rates of reactions to be measured under identical conditions.

To augment the preceding data, some partition measurements were made. Thus, **2** (0.0100 g) was dissolved in $CF_3C_6F_{11}$ (1.00 mL), and equal volumes of THF, acetone, CH_2Cl_2, or toluene were added. The samples were kept at 80 °C for 0.5 h and then cooled with stirring. The phases were carefully separated, and the NMR standard $P(C_6F_5)_3$ was added to each (≥0.0101 g). The quantity of **2** was determined by integration of the ^{31}P NMR signals. Partition ratios were >99.7:<0.3 in each case. Note that the values are derived from measured quantities of three significant digits. The $CF_3C_6F_{11}$/THF experiment was further checked for mass recovery (**2** in $CF_3C_6F_{11}$ phase, 0.0097 g). The nonfluorinated complex **3** was also allowed to partition between $CF_3C_6F_{11}$ and THF or toluene. Ratios were <0.3: >99.7, consistent with the lack of detectable solubility in $CF_3C_6F_{11}$.

2. Solid State Characterization. Surprisingly, **2** and **4** could be crystallized as yellow prisms. To our knowledge, no comparably fluorinated compounds have been crystallographically characterized.[12] The Cambridge Structural Database lists many species with four consecutive CF$_2$ groups, but as illustrated in Chart 1 only two with six or more consecutive CF$_2$ groups.[13] In contrast, **2** and **4** contain *six* segments of *six* consecutive CF$_2$ groups. The structures of perfluoroalkanes are of intense interest.[14] However, study has been hampered by the limited information available from other experimental probes, as well as a lack of crystalline compounds with long CF$_2$ segments. Curiously, despite extensive crystallization attempts, the nonfluorinated complex **3** has remained an oil.

Chart 1. Other Crystallographically Characterized Compounds with (CF$_2$)$_x$ Segments of *n* > 6



The crystal structures of **2** and **4** were determined at −80 °C as outlined in Table 1 and the Experimental Section. Key bond lengths and angles are listed in Table 2, and molecular structures are given in Figure 1. As might be expected, **2** and **4** are isostructural, with nearly identical unit cell dimensions. The unit cell of **2** has a slightly greater volume, consistent with the fractionally larger radius of iridium. The bond lengths and angles about the metals are similar to those of other structurally characterized *trans*-M(CO)(Cl)(PR$_3$)$_2$ complexes. For example, *trans*-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$ exhibits (at room temperature) Ir−P, Ir−Cl, and Ir−C bond lengths of 2.347(2), 2.421(5), and 1.80(2) Å and L−Ir−L bond angles of 90° ± 1° and 180° ± 1°.[15]

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Table 2. Key Bond Lengths (Å) and Angles (deg) in 2 and 4

	2	4
M−Cl	2.361 (2)	2.359 (2)
M−P1	2.307 (2)	2.301 (2)
M−P2	2.311 (2)	2.306 (2)
M−C1	1.783 (7)	1.799 (6)
C1−O1	1.160 (8)	1.157 (7)
P1−C18	1.821 (7)	1.834 (6)
P1−C2	1.828 (6)	1.829 (6)
P1−C10	1.829 (7)	1.831 (6)
P2−C34	1.832 (6)	1.829 (5)
P2−C26	1.834 (7)	1.822 (6)
P2−C42	1.836 (7)	1.839 (6)
C1−M−P2	93.4 (3)	94.1 (2)
C1−M−P1	94.4 (3)	93.7 (2)
C1−M-Cl	179.3 (3)	179.0 (2)
P1−M−P2	172.18 (6)	172.26 (6)
P2−M−Cl	86.46 (7)	86.51 (6)
M−C1−O1	178.9 (8)	179.4 (5)
P1−M−Cl	85.72 (7)	85.75 (6)
C18−P1−C2	104.0 (3)	103.5 (3)
C18−P1−C10	102.2 (3)	102.8 (3)
C2−P1−C10	101.7 (3)	102.1 (3)
C18−P1−M	119.0 (3)	120.1 (2)
C2−P1−M	114.0 (2)	113.5 (2)
C10−P1−M	113.7 (3)	112.7 (2)
C34−P2−C26	103.2 (3)	103.1 (3)
C34−P2−C42	104.5 (3)	104.4 (3)
C26−P2−C42	102.1 (3)	101.8 (3)
C34−P2−M	113.6 (2)	113.0 (2)
C26−P2−M	112.8 (3)	112.9 (2)
C42−P2−M	118.8 (2)	119.9 (2)

The most distinctive features of **2** and **4** involve the six pony tails. Four (commencing at C2, C10, C26, and C34) are essentially parallel and coplanar, with all of the $CX_2CX_2CF_2CF_2$ (X = H or F) segments featuring anti conformations. These define a raft of ca. 21 × 6 Å. The remaining two pony tails (commencing at C18 and C42) extend on a common side of the raft and feature *gauche* turns in the $C\boldsymbol{H}_2CF_2CF_2CF_2$ segments. Also, the CF_2CF_3 end groups have larger thermal ellipsoids and are 20% disordered. In **2**, the torsion angles associated with the $CF_2CF_2CF_2CF_{2-3}$ segments range from 161.7(6)° to 176.9(1.3)°, with an average of 169.0(3.4)°. In **4**, the corresponding values are 161.6(5)°, 175.2(1.2)°, and 168.5(3.2)°. Interestingly, *n*-C_4F_{10} exhibits *three* torsional energy minima, with angles of ca. 166° (most stable), 95° (least stable), and 54°.[14a]

As shown in Figure 1 (bottom), the crystal lattices are comprised of stacks of molecules in which the rafts are paired back-to-back. The resulting assemblies have three layers, with every third layer consisting of four “out of plane” chains from two different metals. This layer is less densely filled, in accord with the slightly disordered CF_2CF_3 groups. The packing motif has the overall effect of maximizing the number of parallel perfluoroalkyl chains in every dimension. However, the separations remain slightly greater than the sum of the van der Waals radii. The van der Waals volumes of the fluorinated and nonfluorinated portions of **2** were calculated, the ratio of which allows the molecule to be rated as “64% fluorous”.

We speculated that the slightly disordered layers might “melt” before the metal-containing layers. Such phase transitions would be revealed by DSC endotherms. However, both **2** and **4** gave sharp melting points (75 and 79 °C),[16] with no decomposition until temperatures above 200 °C. As described below, **2** also survives extended periods in solution at 100−150 °C. The robust nature of these compounds is especially noteworthy in view of the growing precedent for carbon−fluorine bond activation by coordinatively unsaturated metal complexes.[7]

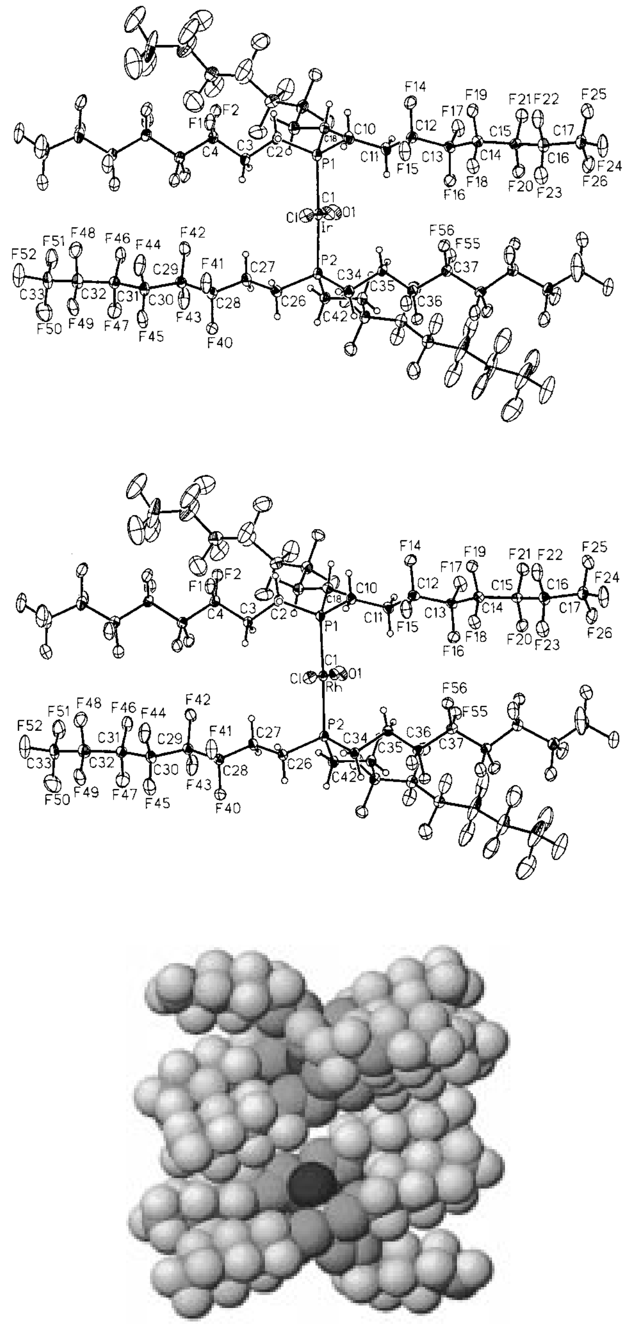

Figure 1. Molecular structure of **2** (top) and **4** (middle), and packing diagram of two molecules of **2**, with non-hydrogen atoms at van der Waals radii (bottom).

3. Reactions with Alkylating Agents. The addition of CH_3I to Vaska’s complex (**1**) involves a S_N2-like mechanism that first gives the cationic iridium salt

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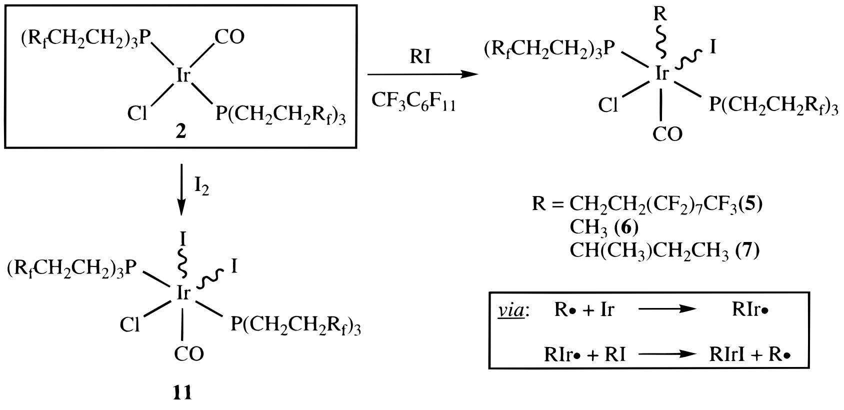
(15) (a) Dahlenburg, L.; Yardimcioglu, A. *J. Organomet. Chem.* **1985**, *291*, 371. (b) There are no complexes of the formula *trans*-M(CO)(Cl)-$[P(\boldsymbol{CH_2}R)_3]_2$ (M = Ir, Rh) in the Cambridge Structural Database.

(16) For the graphical method used to obtain the melting point, see: Cammenga, H. K.; Epple, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1171.

Scheme 2. Reactions of 2 with Alkyl Iodides and I_2



$[Ir(CO)(Cl)(PPh_3)_2(CH_3)]^+I^-$, even in benzene.[8b,17] We thought that such pathways should be disfavored in nonpolar fluorous media. To ensure homogeneous conditions, initial experiments utilized the fluorous iodide $CF_3(CF_2)_7CH_2CH_2I$. As shown in Scheme 2, **2** and $CF_3(CF_2)_7CH_2CH_2I$ (2 equiv) were combined under anaerobic conditions in $CF_3C_6F_{11}$.[18] After 1 h, workup gave the expected alkyl complex $Ir(CO)(Cl)(CH_2CH_2(CF_2)_7CF_3)(I)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**5**) as an analytically pure yellow oil in 84% yield. A ^{31}P NMR spectrum showed three signals (−30.50, −21.35, −20.23 ppm; 73:8:19), which were presumed to represent geometric isomers. The IR ν_{CO} value was higher than that of **2** (2035 vs 1975 cm^{-1}), consistent with an iridium(III) oxidation state.[19]

It was subsequently found that CH_3I also has appreciable solubility in $CF_3C_6F_{11}$. Thus, **2** and CH_3I (4 equiv) were analogously reacted in $CF_3C_6F_{11}$ (Scheme 2). Workup gave the methyl complex $Ir(CO)(Cl)(CH_3)(I)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**6**) in 70% yield and >97% isomeric purity (^{31}P NMR, −23.12 ppm). However, complete reaction required 72 h. We had previously found that PPh_3 and CH_3I react to give the phosphonium salt $[CH_3PPh_3]^+I^-$ much faster than PPh_3 and $CF_3(CF_2)_7CH_2CH_2I$ react to give the fluorinated analogue $[CF_3(CF_2)_7CH_2CH_2PPh_3]^+I^-$.[20] These are presumably one-step S_N2 processes. Hence, the reactions of **2** with CH_3I and $CF_3(CF_2)_7CH_2CH_2I$, which exhibit an inverse rate trend, cannot both involve S_N2 pathways.

To ensure that the two alkyl iodides experienced identical conditions, competition reactions were conducted. Thus **2**, $CF_3(CF_2)_7CH_2CH_2I$, and CH_3I were combined in $CF_3C_6F_{11}$ in a 1:3:3 molar ratio. Only the fluorinated alkyl complex **5** formed, as assayed by ^1H and ^{31}P NMR. We thought it likely that one or both substrates reacted via free-radical chain pathways, as well-documented for **1** and secondary or tertiary alkyl halides and illustrated by the propagation steps in Scheme 2.[21] Accordingly, **5** formed more slowly in the dark or much more rapidly following a brief irradiation. To provide further support, **2**, $CF_3(CF_2)_7CH_2CH_2I$, and CH_3I were combined in the presence of the free-radical trap duroquinone (2:6:6:3 mol ratio; heterogeneous conditions). After 72 h, only **2** and a small amount of a previously unobserved species were detected (95:5, ^{31}P NMR). The rate of reaction of **1** and CH_3I in CH_2Cl_2 is unaffected by duroquinone or galvinoxyl.[21]

These data indicate that in $CF_3C_6F_{11}$, primary alkyl iodides add to **2** via free radical chain pathways. There is an attendant question of whether fluorous solvents give reduced cage effects or intrinsically more favorable environments for such processes. As a probe, **2** and the secondary alkyl iodide $CH_3CH_2(CH_3)CHI$ (4 equiv) were combined under side-by-side conditions in $CF_3C_6F_{11}$ and THF. After 1 h, ^{31}P NMR spectra showed that <1% and 47%, respectively, of **2** remained. A new complex (**7**) cleanly formed in the former reaction (−22.5 ppm). In the latter reaction, two complexes formed (32:21; −20.0, −20.1 ppm), which were tentatively assigned as isomers of **7**. After 18 h, no **2** remained and three complexes were present (56:30:14; −20.0, −20.1, −20.7 ppm). A preparative reaction in $CF_3C_6F_{11}$ gave isomerically pure **7** in 82% yield, which NMR data showed to be the *sec*-butyl complex $Ir(CO)(Cl)(CH(CH_3)CH_2CH_3)(I)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$.

Other alkylating agents were briefly studied. Methyl tosylate has been reported as inert toward **1**[21] and did not react with **2** after 72 h in $CF_3C_6F_{11}$ at room temperature. Methyl triflate adds to **1** in benzene at room temperature[23] and reacted with **2** in both ether and $CF_3C_6F_{11}$. After 14 h, IR spectra showed complete conversion to a new species with a ν_{CO} value of 2062–2065 cm^{-1}. However, upon workup, most of the sample reverted to **2**. Hence, except possibly for the most

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[17] For overviews of the many mechanisms by which alkyl halides can undergo oxidative addition, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 306−322. (b) Henderson, S.; Henderson, R. A. *Adv. Phys. Org. Chem.* **1987**, *23*, 1.

[18] Two side-by-side controls were conducted. In one, **2** and $CF_3(CF_2)_7CH_2CH_2I$ were reacted under standard anaerobic conditions (Experimental Section), and in the other, the **2**/$CF_3C_6F_{11}$ solution was also freeze−pump−thaw degassed. Rates were identical, as monitored by ^{31}P NMR.

[19] The IR ν_{CO} values of the CH_3I, H_2, O_2, and I_2 adducts of **2** (**6**, **8**, **9**, **11**; 2036, 1996, 2021, 2056 cm^{-1} in $CF_3C_6F_{11}$) are sometimes lower than the corresponding adducts of **1** (2048 (Nujol),[8b] 1975 (Nujol),[8b] 2000 (Nujol),[8b] 2071/2069 ($CHCl_3$[8a]/toluene) cm^{-1}), opposite to the trend in Scheme 1. These cases (**6**, **11**) might reflect a different product stereochemistry.

[20] Bernatis, P. Unpublished results, University of Utah.

[21] Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236.

[22] Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541

[23] (a) Strope, D.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 2652. (b) Burgess, J.; Hacker, M. J.; Kemmitt, R. D. *J. Organomet. Chem.* **1974**, *72*, 121.

Scheme 3. Reactions of 2 with H_2 and O_2

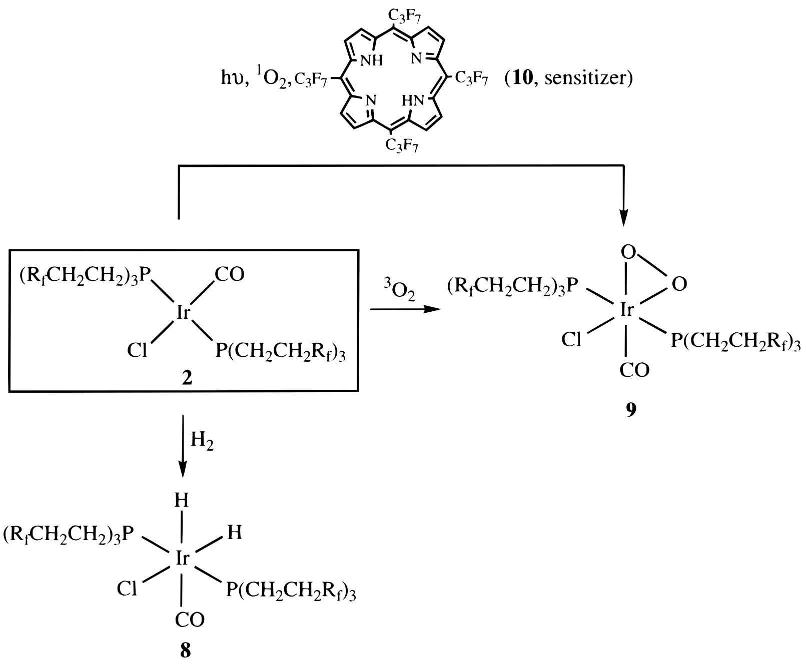

Table 3. Solubility Data for $^3O_2$ and H_2 (25 °C, 1 atm)

property	$CF_3C_6F_{11}$	THF	difference
$^3O_2$ solubility (mol fraction)	0.00456[a]	0.000816[a]	factor of ~5
$^3O_2$ solubility (mol ratio)	0.00453	0.000815	factor of ~5
mol wt (g/mol)	350.05	72.11	factor of ~5
$^3O_2$ solubility (mol/Kg)	0.0129	0.0112	approx equal
density (g/mL)	1.787	0.889	factor of ~2
$^3O_2$ solubility (mol/L)	0.0232	0.0100	factor of ~2
H_2 solubility (mol fraction)	0.0012[b]	0.000274[c]	factor of ~4.5
H_2 solubility (mol ratio)	0.00119	0.000274	factor of ~4.5
H_2 solubility (mol/Kg)	0.0034	0.0038	approx equal
H_2 solubility (mol/L)	0.0061	0.0034	factor of ~2

[a] *IUPAC Solubility Data Series*; Battino, R., Ed.; Pergamon: New York, 1981; Vol. 7, pp 301 and 320. [b] Patrick, C. R. In *Preparation, Properties, and Industrial Applications of Organofluorine Compounds*; Banks, R. E., Ed.; Ellis Horwood: New York, 1982; p 333. [c] *IUPAC Solubility Data Series*; Young, C. L., Ed.; Pergamon: New York, 1981; Vol. 5/6, pp 219 (0.0014007 for *n*-C_7F_{16}, p 243).

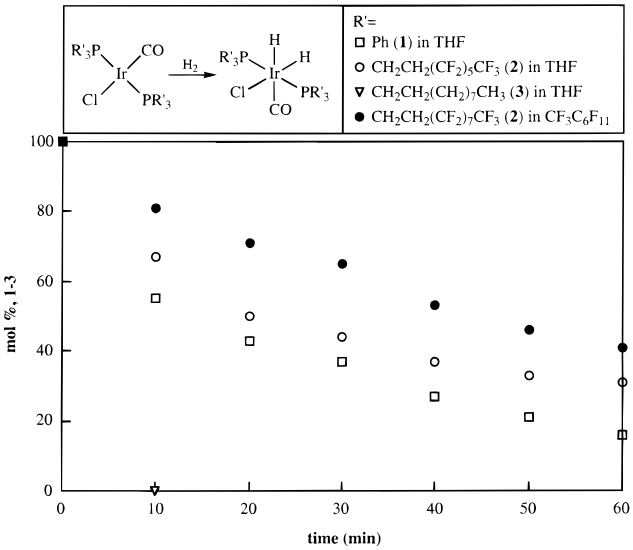

Figure 2. Rates of reaction of **1**−**3** (0.0030 M) and H_2 (0.0034 M in THF or 0.0061 M in $CF_3C_6F_{11}$) at ambient temperature.

reactive alkylating agents, polar addition mechanisms appear to be inoperative with **2** in $CF_3C_6F_{11}$.

4. Reactions with H_2, $^3O_2$, and $^1O_2$. Attention was next turned to nonpolar substrates. As shown in Scheme 3, a $CF_3C_6F_{11}$ solution of **2** was stirred under H_2 (2 atm).[11,24] After 2.5 h, workup gave the dihydride complex $Ir(CO)(Cl)(H)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**8**) as a spectroscopically pure yellow oil in 82% yield. The hydride ligands gave two widely separated ^1H NMR signals (δ −8.97, −19.33), which were coupled to each other and two chemically equivalent phosphorus nuclei (d of t). This requires cis hydride and trans phosphine ligands, per the representation in Scheme 3. Other NMR and IR properties were similar to related compounds described earlier.[25]

Qualitative rate comparisons with the other iridium complexes in Scheme 1 were sought. Thus, three NMR tubes were charged with H_2-saturated, 0.0030 M THF solutions of **1**, **2**, and **3** and capped under 1 atm of H_2. These conditions give starting H_2 concentrations of 0.0034 M (see Table 3). Hence, the relative initial rates are not affected by the rates of H_2 diffusion into solution. The disappearance of **1**−**3** was monitored by ^{31}P NMR, and data are shown graphically in Figure 2. The *n*-octylphosphine complex **3**, which is the most electron rich as judged by the IR ν_{CO} value (Scheme 1), reacted most rapidly (complete within 10 min). Although this trend has much precedent, other data suggest there may be relatively little charge perturbation at iridium or oxidative character to these additions.[24]

Rate effects associated with the fluorous solvent were probed. An NMR tube was charged with a H_2-saturated, 0.0030 M $CF_3C_6F_{11}$ solution of **2** and capped under 1 atm of H_2. Since the molar solubility of H_2 in

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[24] For leading references to H_2 additions to **1**, see: Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147.

[25] See especially compound **10**: Burk, M. J.; McGarth, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034.

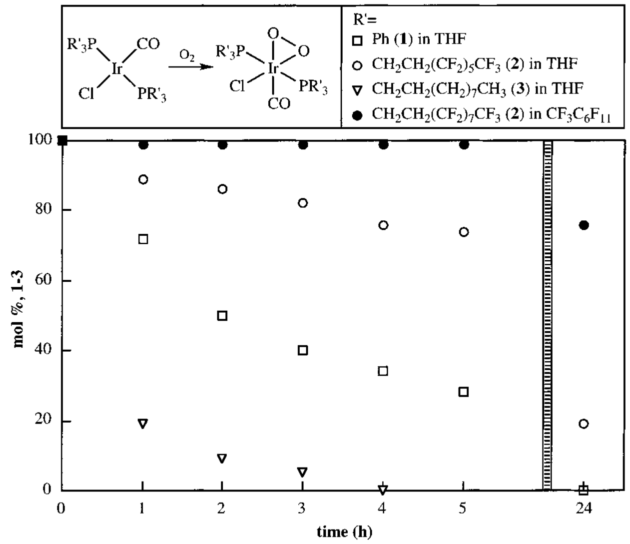

Figure 3. Rates of reaction of **1**−**3** (0.0030 M) and O_2 (0.0100 M in THF or 0.0232 M in $CF_3C_6F_{11}$) at ambient temperature.

$CF_3C_6F_{11}$ (0.0061 M; Table 3) is nearly twice that in THF, a faster reaction might have been expected. However, as illustrated in Figure 2, **2** was consumed more slowly. Hence, the rate constant must be greater in THF. This result is further analyzed in the Discussion section.

As shown in Scheme 3, a $CF_3C_6F_{11}$ solution of **2** was also stirred under $^3O_2$ (2 atm).[11,26] In view of the often-noted high solubilities of oxygen in fluorous solvents,[27] a facile reaction was anticipated. However, the oxygen complex $Ir(CO)(Cl)(O_2)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**9**) slowly formed over the course of 72 h. Workup gave **9** as a yellow oil in 67% yield. Only one ^{31}P NMR signal was observed (1.59 ppm), consistent with the isomer shown in Scheme 3 and literature precedent.[26] The IR ν_{OO} value was slightly greater than that of the O_2 adduct of **1** (864 vs 858 cm^{-1}).[19]

We sought to probe the basis for the sluggish rate. First, three NMR tubes were charged with $^3O_2$-saturated, 0.0030 M THF solutions of **1**, **2**, and **3** and capped under 1 atm of $^3O_2$. These conditions give starting $^3O_2$ concentrations of 0.0100 M (Table 3) or more than a 3-fold excess over **1**−**3**. The disappearance of **1**−**3** was monitored by ^{31}P NMR, and data are summarized in Figure 3. The reactivity order, **3** > **1** > **2**, parallels the electron density on iridium, consistent with an oxidative process. Interestingly, the *perfluoro*triphenylphosphine analogue *trans*-$Ir(CO)(Cl)(P(C_6F_5)_3)_2$ (which has been crystallographically characterized)[26b] is *inert* to $^3O_2$ (ν_{CO} 1994 cm^{-1}).[28] This illustrates the dramatic reactivity consequences possible when reaction centers are not insulated from the perfluorinated moieties by spacer groups.

Next, a $^3O_2$-saturated, 0.0030 M $CF_3C_6F_{11}$ solution of **2** was analogously monitored. Since the molar solubility of $^3O_2$ in $CF_3C_6F_{11}$ (0.0232 M; Table 3) is more than twice that in THF, a faster reaction might have been expected. However, as shown in Figure 3, **2** was consumed much more slowly. Thus, the rate constant must be greater in THF. This trend has been replicated under a variety of conditions (e.g., 3 atm of $^3O_2$ without initial $^3O_2$ saturation) and is further analyzed in the Discussion section. Note also that the molar $^3O_2$ concentrations for the reactions in Figure 3 are greater than the molar H_2 concentrations for the faster reactions in Figure 2. Hence, the rate constants for H_2 addition must be greater than those for $^3O_2$ addition. Accordingly, studies with **1** indicate 10−20-fold differences (benzene or DMF, 20−35 °C, second-order values).[8b]

Foote has shown that the reaction of **1** with singlet oxygen ($^1O_2$) is approximately 10^9 times faster than that with $^3O_2$, consistent with the higher $^1O_2$ ground-state energy.[26b] Furthermore, DiMagno has found that the deep blue 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin (**10**; Scheme 3),[29] which is soluble in fluorocarbons, is an effective photosensitizer for $^1O_2$.[6b,30] Thus, a quartz tube was charged with a 0.005 M $CF_3C_6F_{11}$ solution of **2** and **10** and pressurized with 2 atm of $^3O_2$.[11] The sample was irradiated with a Hanovia 450 W lamp through a long-pass cutoff filter (574 nm). Over the course of 0.5 h, the oxygen complex **9** formed in quantitative yield, as assayed by IR and ^{31}P NMR. Hence, **2** also reacts much faster with $^1O_2$ than $^3O_2$.

5. Other Reactions. To aid in interpreting the above data, additional reactions were conducted. For example, in the alkyl iodide additions, the minor NMR signals attributed to product isomers might possibly arise from the diiodide complex $Ir(CO)(Cl)(I)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**11**).[31] Thus, an authentic sample was sought. As shown in Scheme 2, the reaction of **2** and I_2 in THF gave **11** as an analytically pure orange powder in 72% yield after workup. The ^{31}P NMR spectrum (−41.17 ppm) showed that **11** did not form in any of the preceding reactions.[19]

Phenyl iodide adds to **1** at 140−160 °C in 1-methylnaphthalene or the absence of solvent.[32] In contrast to the reaction of CH_3I and **1**, this is believed to be a nonpolar concerted process. We, therefore, wondered whether similar additions could be effected in fluorous solvents. No reaction occurred when **2** and phenyl iodide (250 equiv) were kept in $CF_3C_6F_{11}$ at 100 °C for 24 h. Thus, **2** and phenyl iodide were similarly kept in perfluorodecalin at 150 °C for 16 h. A ^{31}P NMR spectrum showed that **2** had been consumed, and five new species (two major −29.86, −15.73 ppm; 53:29) were formed. An IR spectrum gave weak bands at 2054 and 2038 cm^{-1}. When **2** was kept in perfluorodecalin at 150 °C for 2 h, no decomposition was evident by IR.

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[26] For leading references to $^3O_2$ and $^1O_2$ additions to **1**, see: (a) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235. (b) Selke, M.; Karney, W. L.; Khan, S. I.; Foote, C. S. *Inorg. Chem.* **1995**, *34*, 5715.

[27] See Riess, J. G.; LeBlanc, M. *Pure Appl. Chem.* **1982**, *54*, 2388 and the references in Table 3.

[28] Vaska, L.; Chen, L. S. *J. Chem. Soc., Chem. Commun.* **1971**, 1080.

[29] (a) DiMagno, S. G.; Williams, R. A.; Therien, M. J. *J. Org. Chem.* **1994**, *59*, 6943. (b) Goll, J. G.; Moore, K. T.; Ghosh, A.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 8344.

[30] For another report of porphyrin-sensitized $^1O_2$ generation in fluorocarbons, see: Chambers, R. D.; Sandford, G.; Shah, A. *Synth. Commun.* **1996**, *26*, 1861.

[31] (a) For data on the I_2 adduct of **1**, see ref 8a and Burke, N. E.; Singhal, A.; Hintz, M. J.; Ley, J. A.; Hui, H.; Smith, L. R.; Blake, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 74. (b) For closely related I_2 adducts, see: Collman, J. P.; Sears, C. T., Jr. *Inorg. Chem.* **1968**, *7*, 27. Yoneda, G.; Blake, D. M. *Inorg. Chem.* **1981**, *20*, 67.

[32] (a) Blum, J.; Weitzberg, M.; Mureinik, R. J. *J. Organomet. Chem.* **1976**, *122*, 261. (b) Mureinik, R. J.; Weitzberg, M.; Blum, J. *Inorg. Chem.* **1979**, *18*, 915.

There is an extensive chemistry of rhodium(I) complexes of the formula *trans*-$Rh(CO)(Cl)(PR_3)_2$.[33] We were curious whether it might be possible to convert **4** to the tris(phosphine) complex $Rh(Cl)[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$ described above.[4] However, in accord with extensive precedent, **4** and $P(CH_2CH_2(CF_2)_5CF_3)_3$ (≥2 equiv) did not react in $CF_3C_6F_{11}$ or THF at room temperature. Other processes occurred upon heating. Attempts to effect substitution using chemical decarbonylating agents were unsuccessful.[34] Also, **4** and $^3O_2$ or $^1O_2$ were reacted under conditions analogous to those in Scheme 3. No oxygen complexes were detected, and ^{31}P NMR spectra showed signals believed to be from the free phosphine oxide (40.1 ppm).[35] Rhodium(I) complexes normally undergo much less rapid additions of $^3O_2$ or $^1O_2$ than iridium(I) complexes.[26b] Other properties of **4** remain under investigation.

Discussion

This study has provided some of the first quantitative structural, solubility, and reactivity data for highly fluorous organometallic complexes. All of the questions posed in the Introduction have to varying extents been addressed. Due to the unexpected crystallinity of **2** and **4**, the lattice packing mode of one type of perfluoroalkyl-rich molecule is now known (Figure 1, bottom).[12] The motif fully supports the “like dissolves like” solvation model proposed as the basis for the immobilization of fluorous catalysts in fluorocarbons.[3]

Accordingly, the partition coefficients measured for **2** in various combinations of $CF_3C_6F_{11}$ and organic solvents are high (>99.7:<0.3). However, the NMR method utilized cannot detect small concentrations, and further studies are in progress. Since **2** is soluble in several organic solvents (Scheme 1), some leaching would be likely after a series of biphase reaction cycles. Hence, the rhodium(I) catalysts being developed in our laboratories feature additional numbers of pony tails and/or longer pony tails.[3−5] Also, since the CH_2CH_2 spacers do not completely insulate the metal from the electron-withdrawing perfluoroalkyl groups, analogous phosphines with additional methylene groups are being prepared and evaluated.[20,35]

In important earlier work, Hughes examined the effect of a single $CH_2CH_2(CF_2)_nCF_3$ substituent ($n = 5$, 7, 9) upon various properties of ferrocene.[6a] He found that solubilities depended upon the length of the perfluoroalkyl group and were a dramatic function of temperature. With $CH_2CH_2(CF_2)_7CF_3$, the n-C_7F_{16}/toluene partition coefficient was 95:5, much lower than those of **2**. Oxidation potentials were 34−38 mV less favorable thermodynamically than that of ferrocene, consistent with a weakly electronegative substituent. However, the IR ν_{CO} values of monocyclopentadienyl complexes $M(CO)_3(\eta^5\text{-}C_5H_4CH_2CH_2(CF_2)_9CF_3)$ indicated that the pony tails were slightly electron *donating*. Hence, in some cases, an XCH_2CH_2 moiety appears sufficient to insulate a metal from a perfluoroalkyl group.

Our data with alkyl iodides (Scheme 2) show that the rates and mechanisms of oxidative additions to coordinatively unsaturated metal complexes can be strongly affected by fluorous media. Previous studies by Kelm are particularly relevant.[36] He measured second-order rate constants for the reaction of **1** and CH_3I at 25 °C in seven solvents ranging in polarity from DMF to toluene. The values decreased by a factor of 11 in this series, and $\Delta V^{\ddagger}$ data strongly supported an S_N2-type mechanism. With **2** in the much less polar solvent $CF_3C_6F_{11}$, there is no evidence for an S_N2 pathway whatsoever, even on time scales of days. Rather, additions occur via an alternative mechanism involving adventitiously initiated free radical chains.[21] In this context, rate constants for radical chain propagation steps in fluorous and organic solvents would be of interest. However, to our knowledge such data are not presently available.

The data in Figures 2 and 3 show that fluorous media can *retard* hydrogenations and oxygenations, despite higher molar H_2 and $^3O_2$ solubilities. Importantly, Kelm also measured second-order rate constants for the reaction of **1** and $^3O_2$ in seven solvents (25 °C).[36] The values decreased by a factor of 6 upon going from DMF to toluene. This was attributed to a slight increase in polarity at the transition state. Available data suggest a parallel but less pronounced trend for reactions of **1** and H_2.[8b] Thus, the rate constants for additions of $^3O_2$ or H_2 to **2** would be expected to be lower in $CF_3C_6F_{11}$ than THF.

We suggest two ways of conceptualizing the effect of the fluorous solvent. The first is to focus on transition state polarity, consistent with Kelm's data and the phosphine rate trends. When the solvent polarity is increased, **2** and $^3O_2$ or H_2 are stabilized less than the transition state. The second is to focus on the apparent ease of formation of cavities or channels in fluorocarbons that can accommodate small nonpolar molecules, as documented by extensive literature on fluorocarbon solvation phenomena.[27] When the solvent is changed to THF, the reactants and transition state are stabilized (better solvated) but the energies of $^3O_2$ or H_2 are affected least. From either viewpoint, the slower reactions in $CF_3C_6F_{11}$ indicate that, relative to the situation in THF, **2** and $^3O_2$ or H_2 are stabilized by $CF_3C_6F_{11}$ more than the transition state.

Additional perspectives on fluorous solvent effects are provided by the gas solubility data in Table 3. Values are normally compiled as mole fractions, a unit not commonly employed by preparative chemists or kineticists. These constitute the origin of the widespread statement that “gases are much more soluble in fluorocarbons”—a generalization appropriate with reference to water but less so for organic solvents.[27] As shown in Table 3, the solubilities of $^3O_2$ in $CF_3C_6F_{11}$ and THF differ by a factor of 5 when expressed as mole fractions (0.00456 vs 0.000816) or nearly equivalent mole ratios (0.00453 vs 0.00815). However, the molecular weights of fluorocarbons tend to be higher than those of organic solvents, and those of $CF_3C_6F_{11}$ and

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[33] (a) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 5, Chapter 35.2.1.4. (b) Sharp, P. R. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1985; Vol. 8, Chapter 2.2.1.3.

[34] O'Connor, J. M.; Ma, J. *Inorg. Chem.* **1993**, *32*, 1866.

[35] Rutherford, D.; Juliette, J. J. J.; Alvey, L. J.; Gladysz, J. A. Manuscript in preparation.

[36] Steiger, H.; Kelm, H. *J. Phys. Chem.* **1973**, *77*, 290.

THF differ by a factor of ca. 5. This gives (0.00453 mol of $^3O_2$)/(350.05 g of $CF_3C_6F_{11}$) and (0.000815 mol of $^3O_2$)/(72.11 g of THF), resulting in nearly equal molal concentrations (mol/Kg; Table 3).

The densities of fluorocarbons also tend to be higher than those of nonhalogenated organic solvents, and those with $CF_3C_6F_{11}$ and THF differ by a factor of 2. This translates the preceding values to (0.00453 mol of $^3O_2$)/(195.9 mL of $CF_3C_6F_{11}$) and (0.000815 mol of $^3O_2$)/(81.1 mL of THF), resulting in molar concentrations that differ by a factor of slightly more than 2 (Table 3). The solubility of H_2 in $CF_3C_6F_{11}$ and THF is slightly lower (0.0012 vs 0.000274 as mole fractions). However, the relationships between molal and molar concentrations turn out nearly the same as with $^3O_2$ (Table 3). Hence, solubility-based rate accelerations for reactions of gases in fluorous (versus organic) solvents must by necessity be modest—a factor not appreciated in the design phase of this study.

Regardless of origin, the preceding selectivity patterns have a number of implications. For example, most reactions of transition metal complexes and CH_3I are believed to involve an initial S_N2 step.[17] Thus, fluorous solvents should retard many reactions involving CH_3I. One such commodity chemical process would be the rhodium-catalyzed, iodide-promoted, conversion of methanol and carbon monoxide to acetic acid.[37] However, slight decreases in the rates of reaction of $^3O_2$ or H_2, as found with **2**, should not limit future applications. Finally, water is an increasingly popular medium for biphase catalysis. In a relevant recent report, Atwood measured second-order rate constants for the reaction of H_2 and a water-soluble analogue of Vaska's complex, *trans*-Ir(CO)(Cl)(TPPMS)$_2$ (TPPMS = P(*m*-$C_6H_4SO_3K$)-Ph_2).[38] The rate constant was comparable to that of **1** in DMSO and an order of magnitude faster in water, consistent with the solvent polarity effects noted above. Extensions to $^3O_2$ and alkyl iodide additions are in progress.

In conclusion, this study has provided heretofore unavailable data and insights regarding the structures of perfluoroalkyl-rich molecules. Effects of phosphine-based fluorous pony tails upon the electronic and solubility properties of representative transition metal complexes have been defined. The fluorocarbon solvent $CF_3C_6F_{11}$ gives marked selectivity changes for addition processes that play pivotal roles in catalysis. Some of these originate from changes in mechanism and others from solvation phenomena. No reactions of any carbon fluorine bonds are detected, even at elevated temperatures. Taken together, these data provide a broad and solid foundation for the design of new fluorocarbon-immobilized reagents or catalysts, several of which will be reported soon.[4b,5]

Experimental Section

General Data. Reactions were carried out under nitrogen atmospheres except in cases of gaseous reactants. IR spectra were recorded on a Mattson Polaris FT spectrometer. NMR spectra were recorded on Varian 300 MHz spectrometers at ambient probe temperature and referenced as follows: ^1H (δ), $Si(CH_3)_4$ (0.00), acetone-d_5 (2.05), or C_6D_5H (7.16); ^{31}P, external 85% H_3PO_4 (0.00 ppm). All coupling constants (J) are in hertz. A Finnigan MAT 95 high-resolution mass spectrometer and T. A. Instruments model 2910 DSC were employed. Microanalyses were conducted by Atlantic Microlab.

THF was distilled from Na/benzophenone. Methyl triflate (Aldrich), $CF_3C_6F_{11}$ (Oakwood), and perfluorodecalin (PCR) were distilled from P_2O_5. The last was freeze−pump−thaw degassed. Other solvents, gases, iridium and rhodium reactants (all from common commercial sources), and the following were used as received: $P(CH_2CH_2(CF_2)_5CF_3)_3$ (Exxon);[3a,b] $P((CH_2)_7CH_3)_3$, $CF_3(CF_2)_7CH_2CH_2I$, $CH_3CH_2(CH_3)CHI$, C_6H_5I, duroquinone, methyl tosylate (Aldrich); CH_3I, I_2 (Mallinckrodt); $P(C_6F_5)_3$ (Strem); 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin (generously supplied by Prof. M. Therien).[29]

Ir(CO)(Cl)[P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]$_2$ (2). A Schlenk flask was charged with $[Ir(Cl)(cod)]_2$ (0.069 g, 0.10 mmol). Then hexane/CH_2Cl_2 (5/5 mL)[10] and $P(CH_2CH_2(CF_2)_5CF_3)_3$ (0.440 g, 0.412 mmol) were added with stirring. After 10 min, CO (1 atm)[11] was added. After 15 min, volatiles were removed by oil-pump vacuum. Ether was added (10 mL), and the sample was filtered. Solvent was removed by rotary evaporation. The light yellow powder was dried by oil-pump vacuum to give **2** (0.479 g, 0.199 mmol, 97%), mp 75 °C (DSC).[16] Anal. Calcd for $C_{49}H_{24}ClF_{78}IrOP_2$: C, 24.52; H, 1.01. Found: C, 24.46; H, 1.07. IR (cm^{-1}, $CF_3C_6F_{11}$/Nujol): ν_{CO} 1975/1975 (s). ^1H NMR (δ, acetone-d_6): 2.80 (m, 6 CH_2), 2.71 (m, 6 CH'_2), $^{31}P\{^1H\}$ NMR (ppm, acetone-d_6/$CF_3C_6F_{11}$): 22.52/18.20 (s).

Ir(CO)(Cl)[P((CH$_2$)$_7$CH$_3$)$_3$]$_2$ (3). A Schlenk flask was charged with $[Ir(Cl)(cod)]_2$ (0.050 g, 0.077 mmol). Then hexane/CH_2Cl_2 (5/5 mL) and $P((CH_2)_7CH_3)_3$ (0.052 mL, 0.147 mmol) were added with stirring. After 10 min, CO (1 atm)[11] was added. After 1 h, volatiles were removed by oil-pump vacuum. Ether was added (10 mL), and the sample was filtered. Solvent was removed by rotary evaporation. The residue was dissolved in hexane (5 mL), and $P((CH_2)_7CH_3)_3$ (0.005−0.010 mL) was added. After 15 min, volatiles were removed by oil-pump vacuum to give **3** as a yellow oil (0.129 g, 0.129 mmol, 84%). Anal. Calcd for $C_{49}H_{102}ClIrOP_2$ with/without (hexane)$_{0.5}$: C, 60.05/59.05; H, 10.56/10.31. Found: C, 60.15; H, 10.45. IR (cm^{-1}, hexane/Nujol): ν_{CO} 1944/1942 (s). ^1H NMR (C_6D_6): δ, 2.20 (m, 6 PCH_2), 1.85 (m, 6 $PCH_2C\boldsymbol{H}_2$), 1.42 (m, 6 $(CH_2)_5$), 1.05 (pseudo t, J_{HH} = 6.7 Hz, 6 CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.2, 27.0−25.2 (br s, m; 1:2, C1−C3), 30.1, 30.0 (2 s, C4, C5), 32.6 (s, C6), 23.5 (s, C7), 14.7 (s, C8).[39] $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): 13.97 (s).

Rh(CO)(Cl)[P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]$_2$ (4). A Schlenk flask was charged with $[Rh(Cl)(cod)]_2$ (0.010 g, 0.020 mmol). Then hexane/CH_2Cl_2 (3/3 mL) and $P(CH_2CH_2(CF_2)_5CF_3)_3$ (0.087 g, 0.081 mmol) were added with stirring. After 10 min, CO (1 atm)[11] was added. After 15 min, volatiles were removed by oil-pump vacuum. Ether was added (10 mL), and the sample was filtered. Solvent was removed by rotary evaporation. The light yellow powder was dried by oil-pump vacuum to give **4** (0.092 g, 0.039 mmol, 98%), mp 79.0 °C (DSC).[16] Anal. Calcd for $C_{49}H_{24}ClF_{78}RhOP_2$: C, 25.47; H, 1.05. Found: C, 25.36; H, 1.12. IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 1979 (s). ^1H NMR (acetone-d_6): δ 2.95−2.86 (m, 6 CH_2), 2.74−2.67 (m, 6 CH'_2). $^{31}P\{^1H\}$ NMR (ppm, acetone-d_6): 27.23 (d, $^1J_{PRh}$ = 120.2 Hz).

Ir(CO)(Cl)(CH$_2$CH$_2$(CF$_2$)$_7$CF$_3$)(I)[P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]$_2$ (5). Method A. A Schlenk flask was charged with **2** (0.100 g, 0.0416 mmol). Then $CF_3C_6F_{11}$ (3 mL) and $CF_3(CF_2)_7CH_2CH_2I$ (0.047 g, 0.082 mmol) were added with stirring.

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[37] Maitlis, P. M.; Haynes, A.; Sunley, G. J.; Howard, M. J. *J. Chem. Soc., Dalton Trans.* **1996**, 2187.

[38] Paterniti, D. P.; Roman, P. J., Jr.; Atwood, J. D. *Organometallics* **1997**, *16*, 3371.

[39] Since a ^{13}C NMR spectrum of free tri(*n*-octyl)phosphine could not be found in the literature, one was recorded for comparison (ppm, C_6D_6): 32.4 (d, J_{CP} = 10.6 Hz, C1), 28.6, 26.5 (2 d, J_{CP} = 14.1, 13.1 Hz, C2, C3), 30.2, 30.1 (2 s, C4, C5), 32.7 (s, C6), 23.5 (s, C7), 14.8 (s, C8). The last three assignments follow from well-established chemical shift patterns in *n*-alkanes and the first from those of *n*-alkylphosphines, see: Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

After 1 h, volatiles were removed by oil-pump vacuum. The residue was washed with CH_2Cl_2 (5 mL), dissolved in ether/pentane (5/5 mL), and chromatographed on silica gel (13 × 1.5 cm column). Solvent was removed from the yellow band by rotary evaporation to give **5** as a yellow oil (0.100 g, 0.033 mmol, 84%). Anal. Calcd for $C_{59}H_{28}ClF_{95}IIrOP_2$: C, 23.83; H, 0.95. Found: C, 23.95; H, 1.01. IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 2035 (s). ^{1}H NMR (C_6D_6): δ 3.0−2.4 (m, 6 PCH_2CH_2), 2.3−2.0 (m, $IrCH_2CH_2$) ^{31}P{^{1}H} (ppm, $CF_3C_6F_{11}$): −30.50 (s, 73.3%), −21.35 (s, 7.6%), −20.23 (s, 19.1%). **Method B.** A Schlenk flask was similarly charged with **2** (0.050 g, 0.021 mmol), $CF_3C_6F_{11}$ (3 mL), and $CF_3(CF_2)_7CH_2CH_2I$ (0.047 g, 0.082 mmol). The sample was kept in the dark and regularly assayed by IR. After 6 h, the formation of **5** was complete.

$Ir(CO)(Cl)(CH_3)(I)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (6). A Schlenk flask was charged with **2** (0.100 g, 0.042 mmol). Then $CF_3C_6F_{11}$ (4 mL) and CH_3I (0.010 mL, 0.17 mmol) were added with stirring. After 3 days, volatiles were removed by oil-pump vacuum. The residue was washed with CH_2Cl_2 (5 mL), dissolved in ether/pentane (5/5 mL), and chromatographed on silica gel (13 × 1.5 cm column). Solvent was removed from the yellow band by rotary evaporation to give **6** as a yellow oil (0.074 g, 0.029 mmol, 70%). Anal. Calcd for $C_{50}H_{27}ClF_{78}IIrOP_2$: C, 23.65; H, 0.95. Found: C, 24.35; H, 1.20.[40] IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 2036 (s). ^{1}H NMR (acetone-d_6): δ 3.28−2.95 (m, 6 PCH_2CH_2), 1.60 (t, $^2J_{PH}$ = 5.3 Hz, CH_3). ^{31}P{^{1}H} NMR (ppm, acetone-d_6): −23.12 (s).

$Ir(CO)(Cl)(CH(CH_3)CH_2CH_3)(I)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (7). A Schlenk flask was charged with **2** (0.025 g, 0.0104 mmol). Then $CF_3C_6F_{11}$ (4 mL) and $CH_3CH_2(CH_3)CHI$ (0.0048 mL, 0.042 mmol) were added with stirring. After 1 h, volatiles were removed by oil-pump vacuum and hexane (5 mL) was added. The solution was cooled to −30 °C and concentrated. A yellow oil formed, which was separated and dried by oil-pump vacuum to give **7** (0.022 g, 0.0085 mmol, 82%). Anal. Calcd for $C_{53}H_{33}ClF_{78}IIrOP_2$: C, 24.63; H, 1.29. Found: C, 26.34; H, 2.51.[40] IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 2052 (s). ^{1}H NMR ($CF_3C_6F_{11}$): δ 4.15 (m, $IrCHC\boldsymbol{H}_2CH_3$), 3.3−2.8 (m, 6 PCH_2CH_2), 1.97 (m, IrCH), 1.43 (d, $^3J_{HH}$ = 6.0 Hz, $IrCHC\boldsymbol{H}_3$), 1.17 (t, $^3J_{HH}$ = 7.2 Hz, $IrCHCH_2C\boldsymbol{H}_3$). ^{31}P{^{1}H} NMR (ppm, $CF_3C_6F_{11}$): −23.34 (s).

Mechanism of RI Addition. The following experiments are representative. **Trial A**. A Schlenk flask was charged with **2** (0.100 g, 0.042 mmol). Then $CF_3C_6F_{11}$ (4 mL), $CF_3(CF_2)_7CH_2CH_2I$ (0.072 g, 0.125 mmol), and CH_3I (0.008 mL, 0.13 mmol) were added. The reaction was monitored by IR. After 1 h, **2** had been consumed and ^{1}H and ^{31}P NMR spectra showed only **5**. **Trial B.** A Schlenk flask was charged with **2** (0.033 g, 0.014 mmol). Then $CF_3C_6F_{11}$ (2 mL), duroquinone (0.004 g, 0.02 mmol), $CF_3(CF_2)_7CH_2CH_2I$ (0.023 g, 0.041 mmol), and CH_3I (0.003 mL, 0.04 mmol) were added. The reaction was monitored by IR. After 72 h, only **2** could be detected. A ^{31}P NMR spectrum (acetone) showed a 95:5 ratio of **2** and a new species (22.74, −25.11 ppm). Additional $CF_3(CF_2)_7CH_2CH_2I$ (0.023 g, 0.041 mmol) and CH_3I (0.003 mL, 0.04 mmol) were added. After 48 h, a weak new IR band was present (2039 cm^{-1}). After an additional 24 h, a ^{31}P NMR spectrum (acetone) showed a 36:64 ratio of **2** and a new species (22.74, −25.11 ppm). **Trial C.** Two NMR tubes were charged with **2** (0.015 g, 0.0062 mmol), $CF_3(CF_2)_7CH_2CH_2I$ (0.014 g, 0.025 mmol), and $CF_3C_6F_{11}$ (0.8 mL). One was irradiated for 15 min (Hanovia 450 W lamp), and the other was kept under ambient light. ^{31}P NMR spectra showed >98% conversion of **2** to **5** immediately after the irradiation period and 10% conversion after 1 h for the other sample.[18] **Trial D.** Separate Schlenk flasks were charged with **2** (0.025 g, 0.010 mmol) and $CH_3CH_2(CH_3)CHI$ (0.025 g, 0.042 mmol) in $CF_3C_6F_{11}$ (2 mL) and **2** (0.025 g, 0.010 mmol) and $CH_3CH_2(CH_3)CHI$ (0.025 g, 0.042 mmol) in THF (2 mL). These were stirred and periodically monitored by ^{31}P NMR. Data: see text.

Other Attempted Alkylations or Arylations. Trial A. A Schlenk flask was charged with **2** (0.025 g, 0.010 mmol). Then $CF_3C_6F_{11}$ (4 mL) and methyl tosylate (0.007 mL, 0.04 mmol) were added with stirring. IR spectra (24, 72 h) showed that no reaction had occurred. **Trial B.** A Schlenk flask was charged with **2** (0.050 g, 0.021 mmol). Then ether (4 mL) and methyl triflate (0.100 mL, 0.168 mmol) were added with stirring. After 14 h, volatiles were removed from the colorless solution by oil-pump vacuum. The residue was washed with hexane (5 mL) to give a colorless oil. IR (cm^{-1}, ether): ν_{CO} 2062 (s). ^{31}P{^{1}H} NMR (acetone, ppm): 3.61 (s, 66%), 22.60 (s, 34%, **2**). A comparable experiment in $CF_3C_6F_{11}$ gave similar results. **Trial C.** Two Schlenk flasks were charged with **2** (0.020 g, 0.0083 mmol). Then $CF_3C_6F_{11}$ or perfluorodecalin (4 mL) and C_6H_5I (0.423 g, 2.08 mmol) were added with stirring. The samples were kept at 100 °C for 20 h and 150 °C for 20 h. Data: see text.

$Ir(CO)(Cl)(H)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (8). A Schlenk flask was charged with **2** (0.050 g, 0.021 mmol). Then $CF_3C_6F_{11}$ (4 mL) and H_2 (2 atm)[11] were added with stirring. After 2.5 h, volatiles were removed by oil-pump vacuum. Ether was added (10 mL), and the sample was filtered. Solvent was removed by rotary evaporation to give **8** as a yellow oil (0.041 g, 0.017 mmol, 82%). Anal. Calcd for $C_{49}H_{26}ClF_{78}IrOP_2$: C, 24.50; H, 1.09. Found: C, 25.83; H, 1.32.[40] IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 1996 (s), ν_{IrH} 2094 (s). ^{1}H NMR (acetone-d_6): δ 2.82−2.66 (m, 6 PCH_2CH_2), −8.97 (td, $^2J_{PH}$ = 18.9 Hz, $^2J_{HH}$ = 4.8 Hz, IrH), −19.33 (td, $^2J_{PH}$ = 13.7 Hz, $^2J_{HH}$ = 4.9 Hz, IrH′). ^{31}P{^{1}H} NMR (ppm, acetone-d_6): 5.65 (virtual d, J = 3.5 Hz).

$Ir(CO)(Cl)(O_2)[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (9) Method A. A Schlenk flask was charged with **2** (0.058 g, 0.024 mmol). Then $CF_3C_6F_{11}$ (4 mL) and $^3O_2$ (2 atm)[11] were added with stirring. After 3 days, volatiles were removed by oil-pump vacuum. Ether was added (10 mL), and the sample was filtered. Solvent was removed by rotary evaporation to give **9** as a yellow oil (0.039 g, 0.016 mmol, 67%). Anal. Calcd for $C_{49}H_{24}ClF_{78}IrO_3P_2$: C, 24.20; H, 0.99. Found: C, 24.70; H, 1.20. IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 2021 (s), 864 ν_{OO} (m). ^{1}H NMR (acetone-d_6): δ 2.82−2.66 (m, 6 PCH_2CH_2). ^{31}P{^{1}H} NMR (ppm, acetone-d_6): 1.59 (s). **Method B.** A thick-walled quartz tube was charged with **2** (0.012 g, 0.0050 mol), 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin[6b,29] (0.005 g, 0.005 mmol), $CF_3C_6F_{11}$, and $^3O_2$ (2 atm). The sample was irradiated (Hanovia 450 W lamp) through a 2.5 cm 1 M K_2CrO_7 long-pass cutoff filter. After 0.5 h, conversion to **9** was complete. IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 2019 (s), 873 ν_{OO} (m). ^{31}P{^{1}H} NMR (ppm, $CF_3C_6F_{11}$): −4.12 (s).

Rates of Reaction of H_2 and $^3O_2$ (Figures 2 and 3). Trial A. Separate 5 mm NMR tubes were charged with **1** (0.0023 g, 0.0030 mmol), **2** (0.0072 g, 0.0030 mmol), and **3** (0.0031 g, 0.0030 mmol), and H_2-saturated THF was added (1.0 mL or 0.0034 mmol H_2 per Table 3; prepared by bubbling H_2 through the THF for 0.5 h, followed by 0.1 h under an H_2 atmosphere). The tubes were capped under H_2 and quickly transferred to NMR probes where ^{31}P spectra were recorded. **Trial B.** A 5 mm NMR tube was similarly charged with **2** (0.0072 g, 0.0030 mmol) and H_2-saturated $CF_3C_6F_{11}$ (1.0 mL, or 0.0061 mmol H_2 per Table 3), capped under H_2, and transferred to a NMR probe. **Trial C.** Trials A and B were repeated on identical scales under $^3O_2$ with $^3O_2$-saturated solvents (0.0100 or 0.0232 mmol $^3O_2$ per Table 3).

$Ir(CO)(Cl)(I)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (11). A Schlenk flask was charged with **2** (0.050 g, 0.021 mmol) and THF (3 mL). The flask was chilled, and I_2 (0.006 g, 0.021 mmol) was added with stirring. After 5 min, solvent was removed by oil-pump vacuum. The residue was extracted with $CF_3C_6F_{11}$ (5 mL). The extract was filtered, and solvent was removed by rotary evaporation. The residue was washed with hexane and

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[40] A correct microanalysis could not be obtained for this oil. The data are presented as one gauge of sample purity.

dried by oil-pump vacuum to give **11** as an orange powder (0.040 g, 0.015 mmol, 72%), mp 98 °C. Anal. Calcd for $C_{49}H_{24}ClF_{78}I_2IrOP_2$: C, 22.18; H, 0.91. Found: C, 22.34; H, 0.98. IR (cm^{-1}, $CF_3C_6F_{11}$): ν_{CO} 2056 (s). $^{31}P\{^1H\}$ NMR (ppm, $CF_3C_6F_{11}$): −41.17 (s).

Partition Coefficients. A 4 mL vial was charged with **2** (0.0100 g, 0.0042 mmol), $CF_3C_6F_{11}$ (1.00 mL), and a second solvent (1.00 mL). The sample was kept at 80 °C for 0.5 h and allowed to cool. The phases were separated by syringe, and solvent was removed by oil-pump vacuum. Each residue was treated with 0.0101−0.0125 g of the standard $P(C_6F_5)_3$ and dissolved in THF. The amount of **2** was determined by integration of the ^{31}P NMR spectra. To help avoid contamination from the phase interface, analyses were also conducted using only 80−90% of the nonfluorous solvent. Data: see text.

Crystallography. Pentane was slowly added to ether solutions of **2** and **4** by vapor diffusion. Yellow prisms formed and were mounted on glass fibers and coated with hydrocarbon oil. Data were collected as summarized in Table 1. Cell constants were obtained from 25 reflections with $22° < 2\theta < 30°$. The space group was determined by least-squares refinement (no systematic absences). Standard reflections showed decay (**2**, 12%; **4**, 3%) during data collection. Anisotropic decay, Lorentz, polarization, and empirical absorption (Ψ scans) corrections were applied. The structures were solved by standard heavy-atom techniques with the MOLEN/VAX package[41] and refined with SHELXL-93 (non-hydrogen atoms anisotropic thermal parameters; hydrogen atom positions calculated, added to the structure factor calculations, and refined using a riding model).[42] Two CF_3CF_2 groups were disordered and refined to an 80:20 occupancy ratio (primed atoms for minor conformation). Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[43,44]

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Supporting Information Available: A table comparing all bond lengths, bond angles, and torsion angles in **2** and **4** (17 pages). Ordering information is given on any current masthead page.

OM9710834

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(44) All data associated with the structures have been deposited in the Cambridge Crystallographic Database.