Inorganic Chemistry

A *cis*-IrL(CO) Group Responds to Increasing Steric Bulk of L by M–L Stretching, Not M–C–O Tilting or Bending

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The crystal structures of [Ir(2-R-bq)(PPh$_3$)$_2$(H)(CO)]$^+$ (bq = benzoquinolinato; R = H, *i*-Pr, *t*-Bu) show that steric interference caused by contact between the bulky pendant R groups of the bq and the C of the *cis*-CO is relieved by Ir–N bond stretching in the Irbq system and bending of the *trans*-Ph$_3$P–Ir–PPh$_3$ groups, rather than by tilting or bending of the CO. Ir–CO is therefore more rigid than the Ir–N and Ir–P bonds. The Ir–N stretching is aided by the presence of a high trans effect H trans to N.

Carbonyls of d^6 metals are generally octahedral and strongly resist deformation from octahedral. Likewise, the M−C−O unit is generally linear and resists deformation. If steric pressure were applied to a carbonyl by a nearby bulky group, two distinct deformations could occur, bending of the M−C−O group at C and tilting of the whole linear M−C−O unit away from the octahedral axis (Figure 1); these could occur separately or together.

A distorted structure was originally proposed for the CO adduct of myoglobin (Mb−CO) and hemoglobin (Hb−CO) as a result of interaction with the bulky distal histidine.[1] Both tilted and bent M−C−O arrangements were considered. Free heme prefers CO to O$_2$ by a factor of ca. 2×10^4 while the proteins show a much lower relative affinity (Hb, 200; Mb, 25).[1] Because FeO$_2$ is bent but FeCO is linear, the distal histidine in Mb and Hb was thought to cause tilting of CO away from the porphyrin ring normal or to cause bending of the M−C−O angle, either of which should disfavor binding of CO relative to O$_2$. The bending angle can be defined as the deviation of the C−O vector from the M−C vector and the tilt angle as the deviation of the M−O vector from the axis of the system.

The area is controversial:[2] some experiments indicate significant bending or tilting in Hb−CO while others do not. For example, both X-ray and neutron diffraction studies[3] of Mb−CO show large distortions (M−C−O = 120°−140°), but vibrational spectroscopy argues for near-linear CO.[4] Ibers has been quoted as saying that "the interpretation of severe
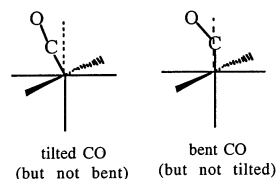

Figure 1. Definitions of bent and tilted CO. The dotted line represents the CO position when undistorted.

bending of FeCO from the original X-ray and neutron Mb−CO structures is something that an inorganic chemist would say is complete nonsense."[5] More recent structural data on Mb−CO indicate a much smaller distortion (tilt = ca. 7°).[6]

Steric effects are important in organometallic chemistry. For example, Grubbs' metathesis catalyst[7a] uses bulky PCy$_3$ rather than PPh$_3$, and metallocene chemistry was transformed by using bulky C$_5$Me$_5$ in place of C$_5$H$_5$.[7b] Steric effects in most such ligands tend to operate in a volume of space much more remote from the metal than the CO in what one can call the γ steric sphere and beyond (see Figure 2). To cause bending or tilting of a ligand like CO that is essentially confined to the $\alpha-\beta$ steric spheres one would need steric

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(1) Collman, J. P.; Brauman, J. I.; Halbertt, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3333.
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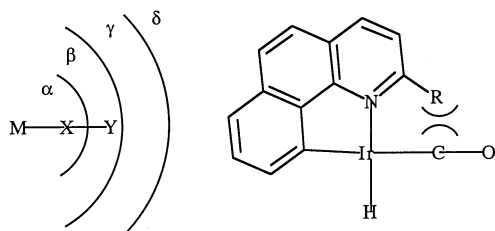
Figure 2. Steric effect of R operates on the C of CO, or in the α sphere. PPh₃ groups have been omitted for clarity.

pressure in the α and β steric spheres.[8] Pressure in the α sphere might destabilize both CO and O₂, so pressure in the β sphere is more likely to be useful for the Hb and Mb cases.
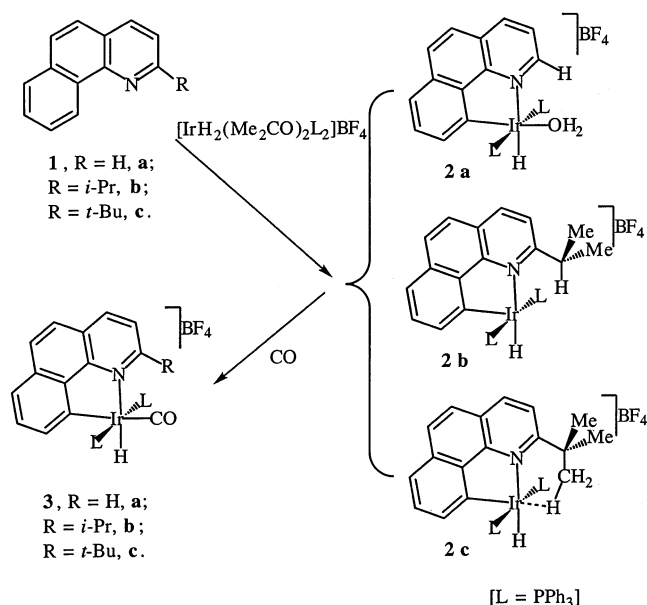
Other systems employ steric effects that probably operate close to the metal. Brookhart's polymerization catalyst[9] uses 2-substituted aryl groups that could have α and β steric effects. Steric effects were originally considered as a global property of a ligand, as most clearly expressed in Tolman's cone angle, a model that considers ligands as a cone.[10a] For PR₃, this model works well, but for irregularly shaped ligands such as ours, we may need to consider the steric spheres in which the effects operate. Coville's[10b] cone angle radial profiles are an example of such an approach.

To see if ligand binding can be controlled by pendant groups in the α–β spheres, we have previously synthesized a series of rigid ligands with pendant hydrogen bonding groups.[11] We now introduce bulky alkyl groups into the 2-position of the rigid chelating benzoquinoline ligand. These cause severe α–β steric effects that have clear consequences on the chemistry of the complexes. In this paper, we look at the effect of such groups on distortions in the CO complexes to determine if CO has any tendency to tilt or bend in this system.

Choice of System and Synthesis of Ligands and Complexes. Benzoquinoline (**1a**) can be readily functionalized at the 2-position to introduce a very wide variety of groups, R. Here, we look at the parent ring system (R = H, **1a**) and the *i*-Pr and *t*-Bu substituted species (R = *i*-Pr, **1b**; *t*-Bu, **1c**). Compound **1a** is commercially available, and we previously[12] made **1b,c** by reaction of benzoquinoline *N*-oxide with LiR.

These benzoquinolines all readily cyclometalate[13] by reaction with the known [IrH₂(Me₂CO)₂L₂]BF₄ (L = PPh₃) at room temperature to give **2a–c** (Scheme 1). Each of these species proves to have a different structure as a result of the change of R. The control case of R = H, the resulting complex **2a**, has a water at the sixth site cis to the bq N (bq = benzoquinolinato). The water ligand results from the presence of moisture in the solvents used. In the case of the

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(9) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem Rev.* **2000**, *100*, 1169.
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Scheme 1

i-Pr species, **2b**, a crystal structure[12] showed that a nonagostic 5-coordinate form is now preferred in the solid state, and spectroscopic data suggest the same structure is maintained in CD₂Cl₂ solution. The factors that disfavor agostic binding in this case have been fully discussed.[13] The *t*-Bu compound **2c** is agostic. Compounds **2a–c** have all been fully characterized in prior work.[12,13]

CO Complexes. We now find that precursors **2b,c** both react readily with CO (1 atm) at room temperature to give 6-coordinate carbonyl complexes, **3b,c**. Analogous complex **3a** was known via another route and previously crystallographically characterized[14] but is also readily accessible in the way we used for **3b,c**, and we have also repeated the crystal structure, but at low temperature, for better comparability with the structures of **3b,c**. Models indicated that the CO in **3a** should be entirely unhindered, so this is taken as the control case. Models also suggest that the *i*-Pr and *t*-Bu groups of **3b,c** should exert significant steric pressure on the CO carbon, and there is no simple way for the ligand to rotate or twist to avoid a direct clash between the R group and the CO. Because the steric pressure seemed likely to be exerted at CO carbon, a tilt rather than a bend was anticipated as the response.

The X-ray crystal structures of **3a–c** (Figures 2–5 and Tables 1 and 2) show the anticipated situation, with CO cis to the bq nitrogen in all cases. Unexpectedly, however, the M–C–O arrangement is very little different in the three cases. The Ir–C–O angle shows no indication of enhanced bending; there is also no increased tilting as indicated by the C(11)–Ir(1)–CO angle. If anything, the IrCO system tends to relax on increasing the steric bulk. The chelating N–Ir–C angle for bq remains the same. The major difference in the structures is not the Ir–C–O group but in the Ir–N bond length. An increase of 0.13 Å in Ir–N was

(14) Neve, F.; Ghedini, M.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1989**, *28*, 3084.
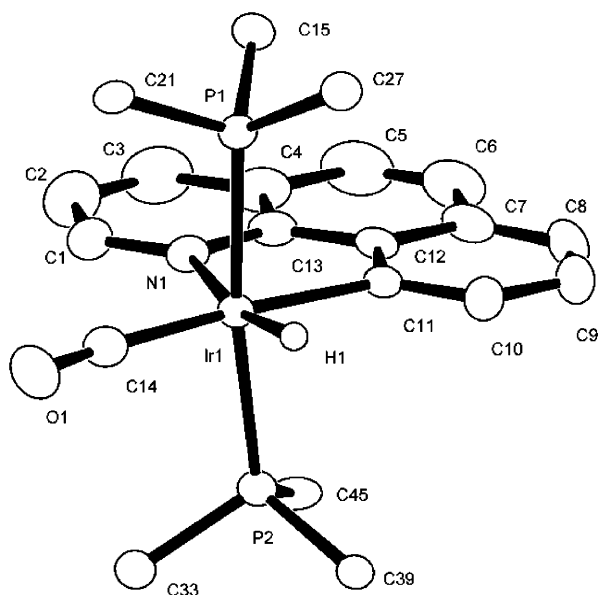
Figure 3. ORTEP diagram of **3a**; only the *ipso*-carbon atoms of the phenyls are shown.
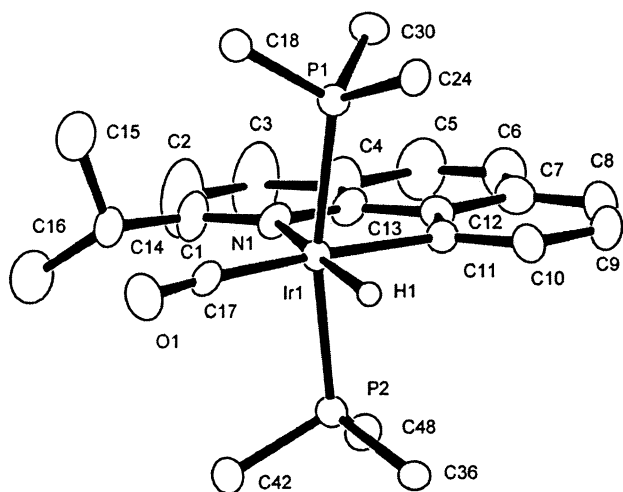

Figure 4. ORTEP diagram of **3b**; only the *ipso*-carbon atoms of the phenyls are shown.

Figure 5. ORTEP diagram of **3c**; only the *ipso*-carbon atoms of the phenyls are shown.

Table 1. Crystallographic Data for **3a**−**c**[a]

	3a	**3b**	**3c**
color, shape	colorless prism	pale yellow plate	colorless plate
empirical formula	$C_{50}H_{39}F_6IrNOP_3$	$C_{53}H_{45}F_6IrNOP_3$	$C_{54}H_{47}BF_6IrNOP_2$
fw	1069.00	1111.08	1066.94
T/K	183	183	183
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
unit cell dimens			
a/Å	14.1296(2)	10.0934(2)	10.1303(2)
b/Å	14.0197(2)	15.4414(3)	15.1748(3)
c/Å	22.5044(3)	29.3713(5)	29.5914(5)
β/deg	103.3213(8)	94.253(1)	93.227(1)
V/Å^3	4337.7(1)	4565.1(1)	4541.7(1)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.637	1.616	1.560
μ/cm^{-1} (Mo Kα)	32.63	31.04	30.76
cryst size/mm^3	0.05 × 0.19 × 0.22	0.10 × 0.24 × 0.24	0.17 × 0.19 × 0.24
total reflns, unique reflns	53778, 10350	28060,10774	33992, 10788
R_{int}	0.070	0.072	0.067
no. obsd ($I > 3\sigma(I)$)	7008	6518	6181
transm range	0.574−0.749	0.523−0.597	0.508−0.865
params, constraints	563, 0	590, 0	581, 0
$R,^b R_w,^c$ GOF	0.026, 0.031, 0.76	0.036, 0.035, 1.11	0.033, 0.036, 0.91
residual density/e Å^{-3}	−1.05 < 0.97	−1.56 < 1.31	−1.04 < 1.50

[a] Monochromatic Mo Kα radiation, 0.71073 Å. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [c] $R_w = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]]^{1/2}$.

observed between **3a** and **3c**. A change is also seen in the phosphines: while the Ir−P bonds are nearly perpendicular to the bq plane in **3a** (P−Ir−P = 172.9°), they are progressively distorted away from the N and CO groups in **3b** (167.9°) and **3c** (164.5°). The overall decrease by 8° in the P−Ir−P angle can most simply be interpreted as a steric effect of the bulky R groups. Instead of being expressed in a tilting of the CO, the steric pressure has instead mainly resulted in an elongation of the Ir−N bond of the bq and a bending of the *trans*-PPh₃ ligands away from R. This has the effect of removing the R group from the vicinity of the CO. The MCO system relaxes as a result of these changes, and if anything, the tilting and bending decrease rather than increase.

The possibility of distortions from the steric interactions was investigated with the molecular mechanics program Cache 5.0 that uses MM3 parameters for most atoms, augmented with additional parameters for an octahedral irid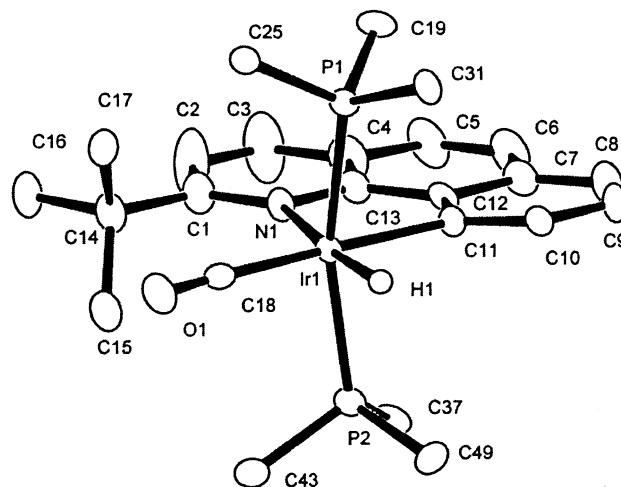ium atom. The results of this generic calculation could provide some insight into the types of distortions that might be expected and which values might be expected to deviate the most. The phosphines were modeled as PH₃. The minimized structures had the metrical parameters shown in Table 3. The trends are in the directions that one might expect, and the MCO system tilts rather more than it bends, with a change in N−Ir−C of 8° from **3a** to **3c** compared to a change in Ir−C−O of only 4.1°. The key difference between the MM prediction and the X-ray data is that the Ir−N bond is stretched much less in the calculation (0.05 Å) than is observed (0.131(10) Å) on going from **3a** to **3c**, but the CO is both tilted (8°) and bent (4.1°) more in the calculation than is observed. The deviations in the absolute values and differences may be the result of the default parameters used for covalent radii and force constants.

No meaningful correlation was observed between IR stretching data and NMR data for **3a**−**c**.

Table 2. Selected Bond Lengths and Angles for Complexes **3a**−**c**

	3a, R = H	**3b**, R = i-Pr	**3c**, R = t-Bu
Bond Lengths (Å)			
Ir(1)−CO	1.937(4)	1.912(5)	1.926(6)
C−O	1.132(4)	1.147(5)	1.129(6)
Ir(1)−N(1)	2.182(3)	2.225(4)	2.313(4)
Ir(1)−H	1.55(5)^a	1.56(6)^a	1.53(5)^a
Ir(1)−P(1)	2.360(1)	2.365(1)	2.359(1)
Ir(1)−P(2)	2.362(1)	2.359(1)	2.379(2)
Ir(1)−C(11)	2.070(3)	2.075(4)	2.087(5)
C(14)···CO		3.158(6)	3.413(7)
^{i}PrH···CO		2.31^b	
Bond Angles (deg)			
Ir(1)−C−O	173.6(3)	174.0(4)	175.0(5)
N(1)−Ir(1)−CO	106.1(1)	104.5(2)	103.7(2)
N(1)−Ir(1)−C(11)	79.0(1)	79.6(2)	79.1(2)
N(1)−Ir(1)−P(1)	89.94(7)	93.6(1)	94.5(1)
N(1)−Ir(1)−P(2)	91.45(7)	92.5(1)	97.3(1)
P(1)−Ir(1)−P(2)	172.95(3)	167.89(4)	164.46(5)
P(1)−Ir(1)−C(11)	88.06(9)	84.1(1)	83.8(1)
P(2)−Ir(1)−C(11)	85.42(9)	86.7(1)	88.5(1)
C(11)−Ir(1)−CO	174.6(1)	175.6(2)	177.2(2)

^{a} The X-ray determination of metrical parameters for metal hydrides is inaccurate. Neutron diffraction generally shows longer bond lengths. ^{b} The separation is based on the X-ray C−H assumed distance of 0.95 Å; the actual separation would be less.

Table 3. Calculated Metric Data (MM3) for **3a**−**c**

	3a (H-bq)	**3b** (i-Pr-bq)	**3c** (t-Bu-bq)
Ir−N (Å)	2.037	2.067	2.086
N−Ir−CO (deg)	95.1	101.1	103.1
Ir−C−O (deg)	179.9	176.9	175.8

Discussion

Because bond bending is generally considered easier than stretching, we expected the CO in the sterically congested systems **3b,c** to tilt to relieve steric strain rather than the M−N distance to stretch. That the reverse occurs suggests that M−CO is a more rigid group than the M−N bond. An additional factor favoring M−N stretching is the high trans influence H trans to N which is expected to favor stretching of the M−N bond of the bq in **3b,c**. This is consistent with other information such as the minimal CO distortion in Hb−CO and Mb−CO and possibly also with the tendency for alkyl and not CO groups to move in migratory insertions to CO. The steric clash may in reality occur between the R group and the PPh$_3$ ligands, with the result that the PPh$_3$ groups bend away from R and the steric pressure on the CO is relieved rather than being increased by the increasing bulk of R on going from **3a** to **c**.

Experimental Section

The syntheses of [Ir(2-t-Bu-bq)(PPh$_3$)$_2$(H)][BF$_4$] and [Ir(2-i-Pr-bq)(PPh$_3$)$_2$(H)][PF$_6$] (**2b**) were described previously.[12]

Bis-triphenylphosphine(2-isopropylbenzoquinolato)hydrido-(carbonyl)iridium(III) Hexafluorophosphate (3b). A solution of the known[12] [Ir(2-i-Pr-bq)(PPh$_3$)$_2$(H)][PF$_6$] (**2b**, 500 mg, 0.462 mmol) in CH$_2$Cl$_2$ (5 mL), in which it is normally insoluble, was prepared as follows. The compound **2b** exhibits limited solubility in many organic solvents following recrystallization,[12] but dissolution may be achieved by the addition of acetone (2 mL) resulting in the formation of a pale yellow solution. Rapid evaporation to dryness leads to a soluble form of the solid, and subsequent addition

of CH$_2$Cl$_2$ (5 mL) to the pale yellow residue results in the formation of a kinetically stable clear orange solution of **2b**. Bubbling CO through this solution at room temperature for 5 min causes a color change to pale yellow. Careful addition of a supernatant layer of diethyl ether (5 mL) and leaving the mixture to stand for 2 days at room temperature results in the accumulation of colorless crystals of **3b**. Yield = 75%, 385 mg. IR (KBr, cm^{-1}): ν 2268 (Ir−H), 2026 (CO). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): d −15.88 (t, $^2J_{H-P}$ = 16.40, 1H, Ir−H), 1.15 (d, J_{H-H} = 8.70, 6H), 3.38 (m, 1H, MeCH), 6.86−7.5 (m, 36H), 8.05 (d, J_{H-H} = 8.65, 1H). ^{31}P{^{1}H} NMR (CD$_2$-Cl$_2$, 202.4 MHz): d 5.03 (s). Anal. Calcd for C$_{53}$H$_{45}$ONP$_3$F$_6$Ir: C, 57.29; H, 4.08; N, 1.26. Found: C, 57.05; H, 3.89; N, 1.21%.

Bis-triphenylphosphine(2-*tert*-butylbenzoquinolato)hydrido-(carbonyl)iridium(III) Tetrafluoroborate (3c). This compound was prepared by the method described for **3b** starting from compound **2c** which is readily soluble in CH$_2$Cl$_2$. Yield = 60%, 308 mg. IR (KBr, cm^{-1}): ν 2274 (Ir−H), 2031 (CO). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): d −17.31 (t, $^2J_{H-P}$ = 15.70, 1H, Ir−H), 1.43 (s, 9H, CH$_3$), 6.95−7.22 (m, 35H), 7.60 (t, J_{H-H} = 8.45, 1H), 7.85 (t, J_{H-H} = 8.56, 1H), 8.05 (d, J_{H-H} = 7.80, 1H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202.4 MHz): d 6.85 (s). Anal. Calcd for C$_{54}$H$_{47}$ONP$_2$-BF$_4$Ir: C, 60.78; H, 4.43; N, 1.31. Found: C, 60.60; H, 4.56; N, 1.23%.

Bis-triphenylphosphine(benzoquinolato)hydrido(carbonyl) iridium(III) Tetrafluoroborate (3a). This known[14] compound was prepared by the method described for **3b,c** starting from [Ir(bq-H)(PPh$_3$)$_2$(H)(H$_2$O)][BF$_4$][13] and, after recrystallization from CH$_2$-Cl$_2$/Et$_2$O, proved to be spectroscopically identical to authentic material. Yield = 80%, 411 mg. IR (KBr, cm^{-1}): ν(Ir−H), 2218 ν(CO) 2048. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): d −15.05 (t, $^2J_{H-P}$ = 14.66, 1H, Ir−H), 6.57−7.56 (m, 38H), 7.95 (d, J_{H-H} = 7.75, 1H), 9.19 (d, J_{H-H} = 7.76). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202.4 MHz): d 7.62 (s)

Structure Determination and Refinement of 3a, 3b, and **3c.** Crystals of **3a** and **3b** were obtained upon crystallization from CH$_2$-Cl$_2$ and diethyl ether. Crystals of **3c** were obtained upon crystallization from CHCl$_3$ and diethyl ether. X-ray data for all three complexes were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV[15]). The structures of **3a** and **3c** were solved by direct methods (SIR92[16]), and the structure of **3b** was solved by Patterson methods.(DIRDIF/Patty[17])- and refined on F for all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions with the exception of the Ir−H that was located in the difference map and refined. The thermal parameters of the counterions of **3a** and **3b** were well behaved. The thermal parameters of the fluorides in **3c** indicated a disorder in the BF$_4$ for which a suitable model was not found; hence, the thermal parameters are large. The structure of **3a** had previously been reported[14] with data collected at room temperature. As we anticipated comparing distances in analogous complexes, the structure of **3a** was redetermined using the same low-temperature

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conditions as **3b** and **3c**. Relevant crystal and data parameters are presented in Tables 1 and 2.