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Rare Organometallic Complex of Divalent, Four-Coordinate Iridium: Synthesis, Structural Characterization, and First Insights into Reactivity[†]

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An application of the new sterically bulky P^O bidentate phosphine $^{t}Bu_2PC(CF_3)_2OH$ (**1**) in the cyclometalation of 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine (**4**) by $IrCl_3$ resulted in the stabilization of unusual coordination states of iridium: from the rare example of a mononuclear, paramagnetic, square-planar Ir^{II} complex, *trans*-$Ir[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2]_2$ (**2**), to a coordinatively unsaturated, five-coordinated monohydride, *trans*-$Ir(H)[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2]_2$ (**3**), and a mono-cyclometalated complex, C^$NIr(H)(CO)[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2]$ (**6**). The complex **2** can be synthesized by two alternative methods: by the aerial oxidation of **3** in the catalytic presence of a base, such as Et_4NOH, or by the sublimation of **3** under vacuum. The Ir^{II} complex **2** undergoes hydrogenation to the $Ir^{III}{-}H$ complex **3**. The reaction between carbon monoxide and a THF solution of complex **2** led to the reduction to the Ir^{I} complex *trans*-$Ir(CO)[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2][\eta^1\text{-}{}^{t}Bu_2PC(CF_3)_2OH]$ (**11**). The C-cyclometalated complex $Ir[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2][\eta^3\text{-}CH_2CMe_2P(^{t}Bu)C(CF_3)_2O]$ (**12**) is formed upon heating of aprotic solutions of complex **2**. The square-pyramidal five-coordinate Ir^{III} hydride **3** reacts with sterically small ligands to form coordinately saturated octahedral species. For example, carbon monoxide forms *trans*-$Ir(H)(CO)[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2]_2$ (**9**) and 4-pyrrolidin-1-yl-pyridine (L) gives *trans*-$Ir(H)(L)[\eta^2\text{-}OC(CF_3)_2P^{t}Bu_2]_2$ (**10**). There is a significant difference in bond lengths between the oxygen and iridium atoms in the divalent state versus the trivalent state for equivalent ligands according to X-ray analysis. Divalent iridium has an average $Ir^{II}{-}O$ distance of 1.970(2) Å, while trivalent iridium has an average $Ir^{III}{-}O$ distance of 1.996(2) Å. The reinvestigation of the original claim in the 1970s on the isolation of a square-planar Ir^{II} complex in the reaction between the phosphine $^{t}Bu_2PC_6H_3(OMe)_2$-2,6 (**15**) and $IrCl_3$ in 2-propanol resulted in the isolation of two square-pyramidal, five-coordinate Ir^{III} hydrides: *trans*-$Ir(H)[\eta^2\text{-}OC_6H_3(^{i}Pr\text{-}6)(OMe\text{-}3)P^{t}Bu_2]_2$ (**16**) and *trans*-$Ir(H)[\eta^2\text{-}OC_6H_2(OMe\text{-}3)P^{t}Bu_2]_2$ (**17**). The X-ray analysis of **17** reveals that the triclinic unit cell parameters are in agreement with the published room-temperature unit cell for the Ir^{II} complex. Bond lengths between the iridium and oxygen atoms in **17** and in the published Ir^{II} complex are 2.012(3) and 2.00 Å, respectively. This falls into our range for red Ir^{III} complexes. The ^1H NMR spectrum of **17** shows a characteristic upfield triplet for $Ir^{III}{-}H$ at δ −48.0 (t, $^2J_{P,H} = 11.9$ Hz). The aerial oxidation of **16** in the catalytic presence of base led to the paramagnetic Ir^{IV} complex $Ir[\eta^3\text{-}OCH_2CMe_2P(^{t}Bu)C_6H_3(^{i}Pr\text{-}6)(OMe\text{-}3)\text{-}O]_2$ (**20**).

Introduction

Smithson Tennant discovered the element iridium 200 years ago in the black residues remaining from the treatment of platinum ores.[1] Since then, iridium has been linked to phenomena ranging from the disappearance of dinosaurs[2] to organic light emitting diodes.[3] Its coordination chemistry has been extensively studied, along with that of other platinum-group metals. However, classical mononuclear complexes with a crystallographically confirmed Ir^{II} oxidation state are extremely rare and are mostly described as intermediates.[4] Stable Ir^{II} complexes stabilized by bulky dianionic porphyrinate ligands exist as nonbridged metal−metal-bound dimers.[5] Two stable Ir^{II}−olefin complexes with distorted-square-pyramidal geometry and one dianionic

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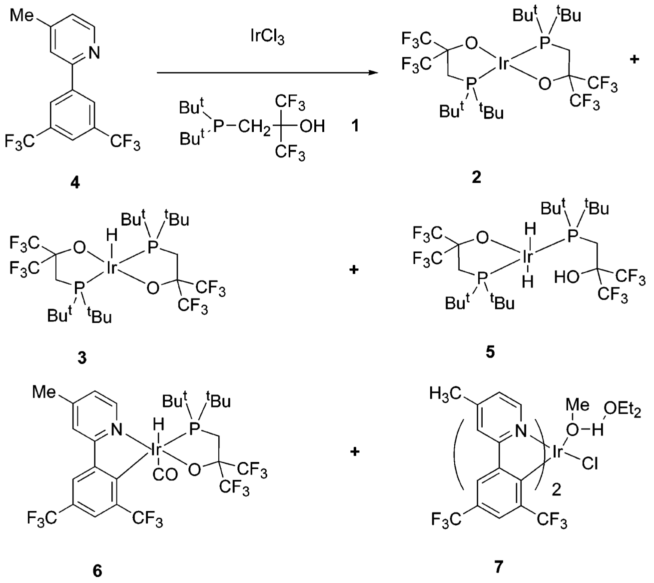
Scheme 1



square-planar Ir^{II} complex were recently reported.[6] Two square-planar Ir^{II} complexes stabilized by P^O bidentate ligands were claimed solely on the basis of X-ray analysis of deep red crystals of this substance, without EPR data to confirm the unusual divalent oxidation state.[7] The red or purple colors of such species are often associated with coordinately unsaturated five-coordinated monohydrides of Ir^{III}–H and differ from Ir^{II} by only one hydrogen atom bound to the iridium, which can be difficult to pinpoint by X-ray analysis,[8] due to the weak scattering factors of hydrogen relative to iridium.

In this report we describe the application of the new sterically hindered chelating phosphine **1** to Ir^{III} chemistry, which resulted in the isolation of the stable square-planar Ir^{II} complex **2** together with the related Ir^{III}–H complex **3**. The structural and chemical differences between these Ir^{II} and Ir^{III}–H complexes were also discovered for the first time.

Results and Discussion

In our search for the stabilization of mono-cyclometalated instead of bis-cyclometalated products for blue luminescent materials in the reaction of 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine (**4**) with Ir^{III} chloride dissolved in ethoxyethanol, we decided to investigate the P^O bidentate species 2-[(di-*tert*-butylphosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol (**1**) as a ligand. The reaction shown in Scheme 1 gives a complex mixture of products, each of which has been structurally characterized.

The mono-cyclometalated complex **6** was isolated and had deep blue photoluminescence with a wavelength maximum at 445 nm. The Ir^{II} complex **2** and Ir^{III}–H complex **3** were separated by chromatography as light blue and red crystals, respectively. Complexes **2** and **3** easily form mixed compositions with different hues, most often purple. The purple color is a result of the combination of blue and red colors. The ORTEP drawings of complexes **2** and **3** are shown in Figures 1 and 2.

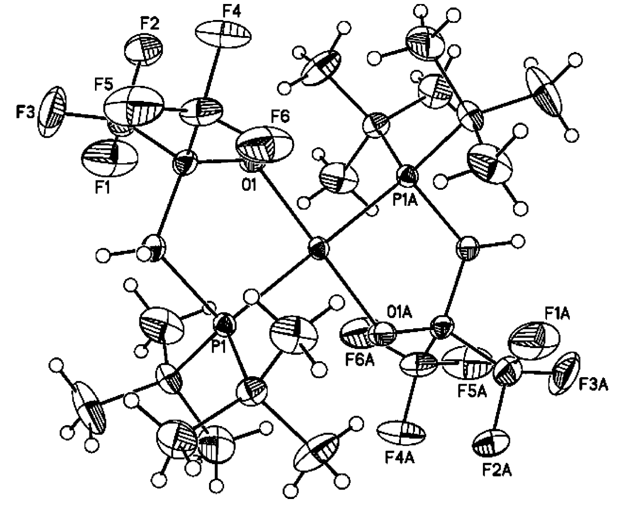


Figure 1. ORTEP drawing of the Ir^{II} complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ir–O = 1.970(2), Ir–P = 2.3038(6).

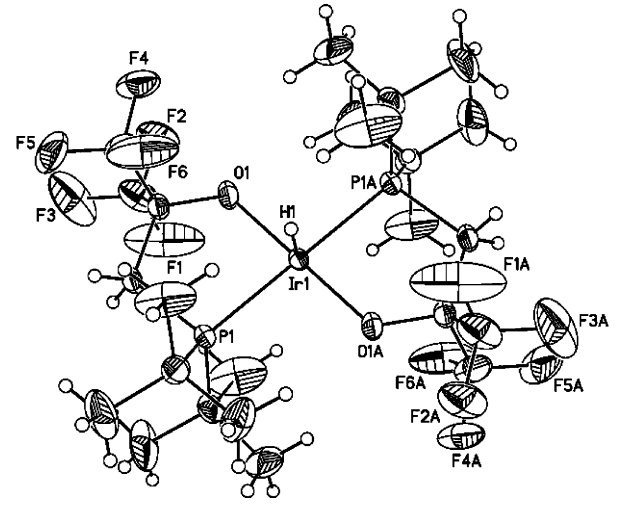


Figure 2. ORTEP drawing of the Ir^{III}–H complex **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ir–O = 1.996(1), Ir–P = 2.3042(8).

The phosphorus and oxygen atoms are perfectly coplanar with the iridium atom, due to an inversion symmetry in both complexes **2** and **3**. There is no substantial change in bond lengths between the phosphorus and iridium atoms in the divalent state versus the trivalent state for equivalent ligands (Table 1). However, there is a significant difference in bond lengths between the oxygen and iridium atoms. Divalent

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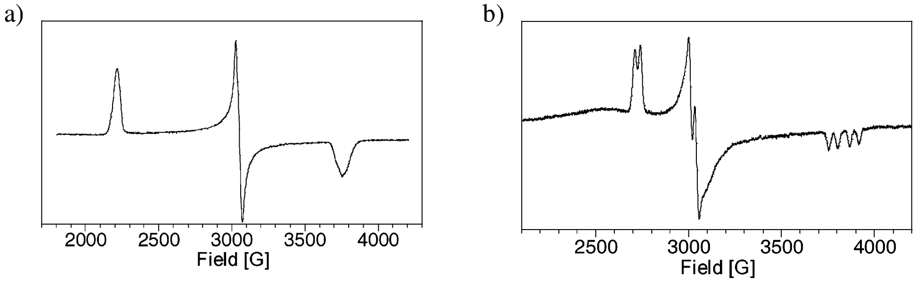

Figure 3. ESR powder spectra of compounds (a) **2** and (b) **20** obtained at 100 K in 2-methyltetrahydrofuran glasses.

Table 1. Selected Bond Lengths (Å) for Compounds 2, 3, 16, and 17

compd	color	bond length Ir−O	bond length Ir−P
2 (3 samples)^a	blue	1.970(2)	2.3038(6)
2 + **3** (2 samples)^a	purple	1.978(1)	2.3077(8)
3 (3 samples)^a	red	1.996(1)	2.3042(8)
16	red	2.028 (4)	2.3272(16)
17^b	red	2.012(3)	2.3100(10)
17 reported as Ir^{II} ^{b}	Red	2.00	2.306

^{a} After averaging. ^{b} Crystal unit cells are equal. Reported data were acquired at room temperature. Our parameters are as follows: triclinic, $P\bar{1}$, a = 8.1966(8) Å, b = 8.6598(9) Å, c = 12.0745(12) Å, α = 78.081(2)°, β = 88.833(2)°, γ = 69.744(2)°, V = 785.50(14) Å^3, Z = 1, T = −100 °C.

iridium has an average Ir^{II}−O distance of 1.970(2) Å, while trivalent iridium has an average Ir^{III}−O distance of 1.996(2) Å. The differences were also consistent, as all of the blue Ir^{II}−O distances were similarly shorter than the red Ir^{III}−O distances. This could be due to the unusually strong cis influence of the hydride in **3**.

Due to the inversion center, the hydride bonded to the iridium for **3** is disordered half above and half below the central plane. Because of the weak scattering factors for hydrogen versus iridium, the half-hydride position for **3** could not be found by X-ray diffraction, either by difference Fourier or by placing and refining. In the final refinement it was fixed 1.62 Å above and below the iridium, on the basis of similar Ir−H bond lengths in the Cambridge database. There are no short contacts found for the idealized hydride of complex **3**. The divalent iridium complex **2** does not have the extra hydride bonded to the iridium.

As expected for d^7 species, complex **2** is paramagnetic (Figure 3, spectrum a). The spectrum contains three distinct g factor values: g_1 = 3.06, g_2 = 2.22, and g_3 = 1.80. Similar parameters were recorded for other Ir^{II} derivatives.[4a,c,6a,8a,d,e] Additional analysis of the ESR spectrum of **2** is beyond the scope of this report. Despite the paramagnetism of **2**, ^{1}H and ^{19}F NMR spectra could be recorded, but ^{13}C and ^{31}P NMR spectra could not, perhaps because protons and fluorine atoms are located further away from the paramagnetic metal center than carbon and phosphorus atoms. The ^{1}H NMR spectrum of **2** contains two broad signals: one at δ 1.20, corresponding to *tert*-butyl groups, and a second at δ 24.10, corresponding to methylene protons with proper integration between them. The ^{19}F NMR spectrum of **2** contains a broad signal at δ −58. The chemical shift value for trifluoromethyl groups is shifted downfield from the usual range by about 20 ppm. A similar phenomena was recorded for porphyrin-based Ir^{II} complexes.[5b]

The square-pyramidal, five-coordinate Ir^{III} hydride **3** is diamagnetic, and it has a characteristic hydride resonance in the ^{1}H NMR spectrum at δ −47.7 (t, $^2J_{P,H}$ = 12.5 Hz). The ^{31}P NMR spectrum of **3** consists of a doublet at δ 80.27 with the same phosphorus−hydrogen coupling constant. The ^{19}F NMR spectrum of **3** contains two quartets at δ −75.37 and −76.51 ($^4J_{F,F}$ = 12.5 Hz).

To shed light on a mechanism for the formation of the square-planar Ir^{II} complex **2**, the following experiments were carried out. Compound **3** was prepared in high yields by the alternative method shown in Scheme 2. Both **2** and **3** have been found to be stable in air at ambient temperature and can be stored indefinitely without decomposition. Remarkably, the catalytic presence of base, such as Et$_4$NOH or even NaOH, led to quantitative aerial oxidation of a THF solution of hydride **3** to complex **2**. Perhaps, the trans influence of a hydroxide anion as a ligand makes the hydride ligand more susceptible to oxidation of the coordinately saturated anionic iridium monohydride[8b] intermediate formed from addition of hydroxide to complex **3**. The second explanation of the catalytic effect of the hydroxide on the transformation of hydride **3** to complex **2** may be the deprotonation of **3** to give an anionic Ir^I intermediate, which is readily oxidized by oxygen to Ir^{II} in a redox reaction. However, the reaction of hydride **3** with a base such as 4-pyrrolidin-1-ylpyridine under anaerobic conditions did not result in such a deprotonation complex (Scheme 2). The complex **2** can be prepared by the second alternative method. The slow sublimation of complex **3** for 120 h at 1 mm and 190 °C produced compound **2** in 59% yield.

Additionally, the square-pyramidal five-coordinate Ir^{III} hydride **3** reacts with sterically small ligands to form coordinately saturated octahedral species. For example, carbon monoxide forms the saturated complex **9** and the aforementioned 4-pyrrolidin-1-ylpyridine gives the stable colorless complex **10** at room temperature (Figure 4). Pyridine, which is less basic then 4-pyrrolidin-1-ylpyridine,[9] forms the corresponding saturated complex in a neat solution of pyridine at reflux, but the starting Ir^{III} hydride **3** precipitates out of solution upon cooling to ambient temperature.

Conversely, the Ir^{II} complex **2** does not react with 4-pyrrolidin-1-ylpyridine under the same conditions used for the Ir^{III} hydride **3**. The reaction between carbon monoxide and a THF solution of Ir^{II} complex **2** led to reduction to a different Ir^I complex, **11** (Scheme 3). The similar tendency of divalent iridium to reduce to uni-

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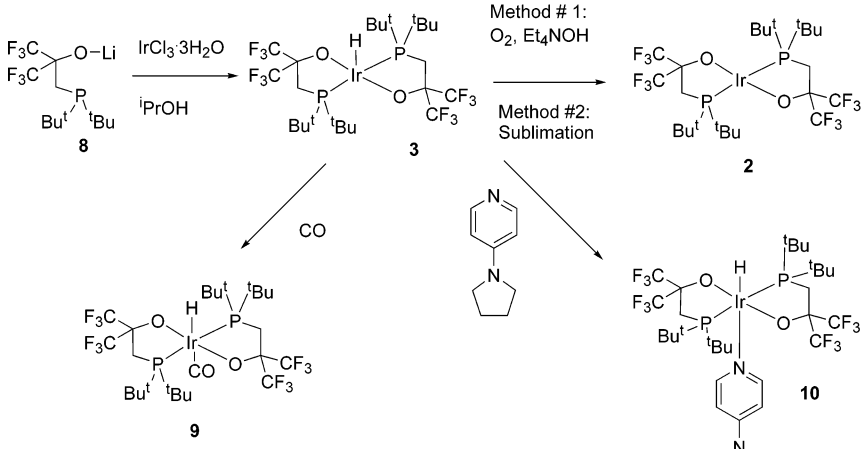
Scheme 2



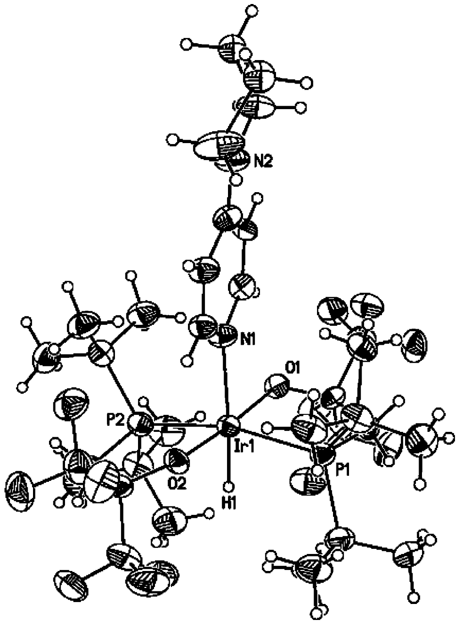


Figure 4. ORTEP drawing of complex **10**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ir−O1 = 2.076(5), Ir−O2 = 2.067(5), Ir−P1 = 2.332(2), Ir−P2 = 2.327(2), Ir−P1 = 2.233(6).

valent status upon reaction with carbon monoxide was recorded for the dianionic square-planar Ir^{II} complex.[6c]

The hydrogenation of the Ir^{II} complex **2** to the Ir^{III}−H complex **3** takes place under rather harsh conditions (700 psig of H_2, 12 h). No further hydrogenation to Ir^{V} hydrides was observed.[8e] C-cyclometalation of one of the methyl groups of **2** occurs upon heating of aprotic solutions of complex **2**. Trimethyl phosphate was found to be the most convenient solvent for this process, because the resulting coordinately unsaturated Ir^{III} complex **12** crystallized out of the solutions cleanly. ^{1}H and ^{13}C NMR spectroscopic parameters for the metalated CH_2−Ir fragment of compound **12** stand out. The ^{1}H NMR spectrum of **12** shows one doublet at δ 3.80 for one hydrogen and a doublet of doublets of doublets for the other hydrogen atom at δ 3.54. This shows that one of the hydrogen atoms couples with both phosphorus nuclei, whereas the other gives rise only to the expected geminal coupling.[10] The ^{13}C NMR spectrum of **12** for the CH_2−Ir fragment shows an upfield doublet at $\delta = -5.3$ (d, $^{2}J_{P,C} = 23.0$ Hz). A two-dimensional ^{1}H and ^{13}C NMR experiment correlates the above signals. It should be noted that the first publication about a square-planar Ir^{II} complex assigned a CH_2−Ir moiety in the ^{1}H NMR spectrum of a related compound to a "complex multiplet in the 2−0.5 ppm region".[7b] As an example of coordinately unsaturated complexes, the red complex **12** reacts with carbon monoxide to yield the colorless adduct **13**. Complex **12** is stable to air at room temperature. Exposure of **12** to air at high temperature results in the formation of the Ir^{IV} binuclear cluster **14**. The C-cyclometaled CH_2−Ir moiety was not affected by the oxidation. The oxidation of phosphorus and iridium atoms took place.

Having proven structural and chemical differences between our Ir^{II} complex **2** and the Ir^{III}−H complex **3**, we decided to reinvestigate the original claim on the isolation of square-planar Ir^{II} complexes stabilized by P^O bidentate ligands.[7] An extensive analysis of the literature posed several contradictory issues. For example, an analogous Rh^{II} complex stabilized by the same di-*tert*-butyl(2-methoxyphenyl)phosphine ligand was described as intensely blue and not a red substance.[11] The same research group in their last publication[12] on this issue reported a "royal blue" Rh^{II} complex stabilized by 2-(di-*tert*-butyl-phosphanyl)-1-phenylethanone. The application of the same ligand to iridium chemistry resulted in the isolation of thermally stable purple unsaturated five-coordinated Ir^{III}−H complexes only. The authors could not prepare the corresponding Ir^{II} complexes by aerial oxidation.

Refluxing the solution of di-*tert*-butyl(2,6-dimethoxyphenyl)phosphine (**15**) and Ir^{III} chloride in 2-propanol for 66 h, as suggested,[7b] resulted in the formation of the red unsaturated five-coordinate Ir^{III}−H complex **16**, with two extra isopropyl groups in position 6 of the ligands (Scheme 4). Refluxing the same components for shorter times (24 h) produced the red unsaturated five-coordinated Ir^{III}−H complex **17** without additional isopropyl groups. This is an interesting example, where

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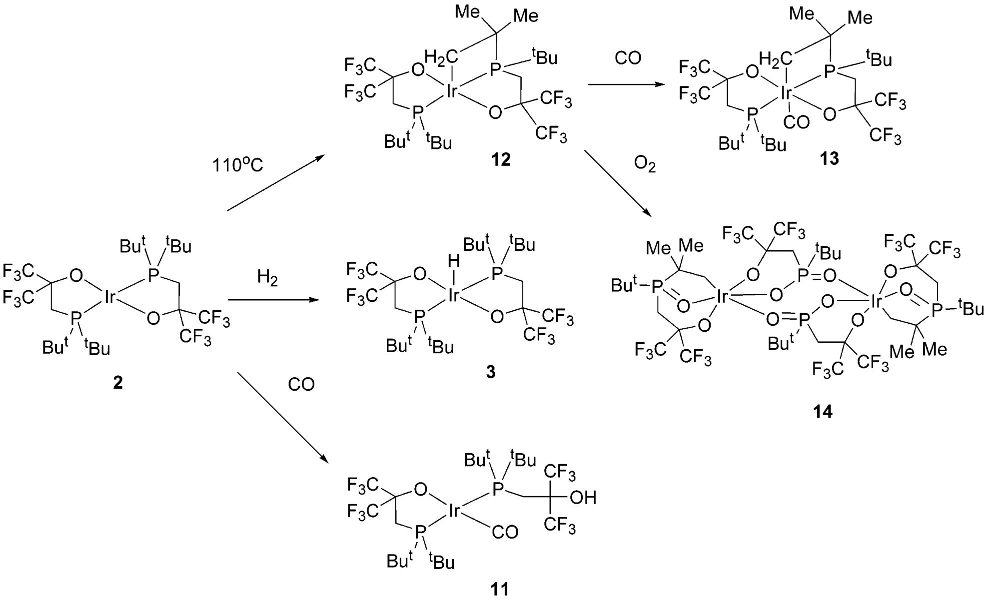
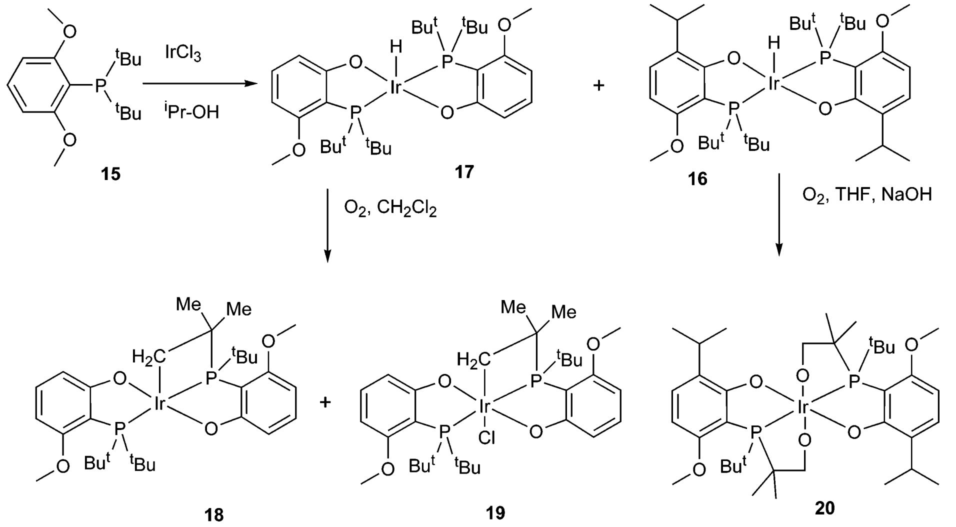
Scheme 3



Scheme 4



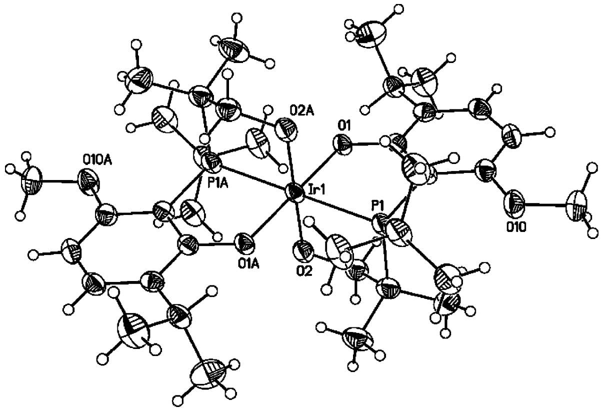


Figure 5. ORTEP drawing of complex **20**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ir−O1 = 2.001(2), Ir−O2 = 1.978(2), Ir−P1 = 2.3378(7).

coordinately unsaturated complex **17** may behave as a Lewis acid catalyst in self-Friedel−Crafts alkylation by 2-propanol or the remaining Ir^{III} chloride may work as a catalyst for the alkylation of the aromatic rings of the ligands. We did not pursue the mechanism any further.

The X-ray analysis of a red crystal of **17** reveals that the triclinic unit cell parameters are in agreement with the published room-temperature unit cell for the Ir^{II} complex (Table 1).[7a] Bond lengths between the iridium and oxygen atoms in **17** and in the published Ir^{II} complex are 2.012(3) and 2.00 Å, respectively. This falls into our range for red Ir^{III} complexes. The ^{1}H NMR spectrum of **17** shows a characteristic upfield triplet for Ir^{III}−H at δ −48.0 (t, $^2J_{P,H}$ = 11.9 Hz). The aerial oxidation of a methylene chloride solution of **17**, as recommended[7b] for the preparation of the Ir^{II} complex, resulted in the formation of the C-cyclometalated Ir^{III} complex **18** and the chlorinated paramagnetic Ir^{IV} complex **19**. The application of our oxidation procedure to complex **16** led to the chlorine-free paramagnetic Ir^{IV} complex **20** (Figures 3 and 5). It is likely that the last two experiments generated transient Ir^{II} complexes, which were stabilized by different routes. The mechanism for the formation of **20** includes, perhaps, coordination of O_2 and the formation of two C−O bonds by intramolecular activation of C−H bonds. To our knowl-

Table 2. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters of 1−3, 5, and 6

	1	**2**	**3**	**5**	**6**
empirical formula	$C_{12}H_{21}F_6OP$	$C_{24}H_{40}F_{12}IrO_2P_2$	$C_{24}H_{41}F_{12}IrO_2P_2$	$C_{24}H_{43}F_{12}IrO_2P_2$	$C_{32}H_{41}F_{12}IrNO_2P$
fw	326.26	421.35	421.85	845.72	922.83
cryst color, form	colorless, irreg block	lt blue, irreg block	red, irreg block	gold, irreg	colorless, parallelogram plate
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.0820(10)	11.2296(17)	11.2311(19)	9.4912(8)	9.4579(8)
b (Å)	11.1281(10)	9.6565(14)	9.6227(17)	21.647(2)	13.6204(12)
c (Å)	8.7645(10)	14.819(2)	14.919(3)	15.9761(15)	14.8067(13)
α (deg)	100.75(2)	90	90	90	73.9130(15)
β (deg)	113.690(10)	106.727(2)	107.020(4)	105.1486(19	74.5780(15)
γ (deg)	69.830(10)	90	90	90	84.4410(15)
V (Å^3)	760.21(14)	1539.0(4)	1541.7(5)	3168.3(5)	1766.2(3)
Z	2	4	4	4	2
density (g/cm^3)	1.425	1.819	1.817	1.773	1.735
abs μ (mm^{-1})	0.237	4.536	4.528	4.407	3.919
F(000)	340	830	832	1672	912
cryst size (mm)	0.34 × 0.34 × 0.32	0.13 × 0.17 × 0.17	0.23 × 0.25 × 0.26	0.20 × 0.28 × 0.28	0.04 × 0.15 × 0.24
temp (°C)	−100	−100	−100	−100	−100
scan mode	ω	ω	ω	ω	ω
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	24.1	28.26	33.14	28.3	28.29
no. of obsd rflns	6413	21 736	29 112	14 574	27 387
no. of unique rflns	2232	3754	5137	7292	8389
R_{merge}	0.0713	0.0299	0.0204	0.019	0.0306
no. of params	191	193	193	394	455
S^a	1.005	1.063	1.097	1.026	1.022
R indices ($I > 2\sigma(I)$)^b	wR2 = 0.1070 R1 = 0.0386	wR2 = 0.0365 R1 = 0.0169	wR2 = 0.0546 R1 = 0.0234	wR2 = 0.0487 R1 = 0.0210	wR2 = 0.0584 R1 = 0.0232
R indices (all data)^a	wR2 = 0.1091 R1 = 0.0414	wR2 = 0.0395 R1 = 0.0244	wR2 = 0.0621 R1 = 0.0348	wR2 = 0.0516 R1 = 0.0274	wR2 = 0.0606 R1 = 0.0269
max diff peak, hole (e/Å^3)	0.242, −0.320	1.105, −0.529	1.905, −1.024	1.442, −0.433	1.745, −0.532

[a] GOF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of refined parameters. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w2).

edge, this is the first example of an iridium compound in which such a process has been demonstrated. The Pd^I-Pd^I dimer is known to undergo a similar sequence of the transformation.[13] An example of an organometallic Ir^{IV} complex containing two catecholate ligands was published.[14]

In conclusion, the application of the new P^O chelating phosphine **1** with a sterically bulky ”soft” di-*tert*-butylphosphine center and sterically bulky ”hard” bis(trifluomethyl)methoxy center resulted in the stabilization of the stable monomeric Ir^{II} complex **2** with classical square-planar geometry described for d^7 complexes akin to Co^{II} and Rh^{II} derivatives. Experiments directed toward the stabilization of other unusual coordination states of transition metals by phosphane **1** are under way in our laboratory.

Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. Di-*tert*-butylphosphine, 3,5-bis(trifluoromethyl)phenylboronic acid, 2-chloro-4-methylpyridine, cesium fluoride, cesium carbonate, tris(dibenzylideneacetone)dipalladium(0), tetraethylammonium hydroxide as a 40% solution in water, 4-pyrrolidin-1-ylpyridine, 1,3-dimethoxybenzene, 1.6 M butyllithium in hexane, and di-*tert*-butylchlorophosphine were purchased from Aldrich. Iridium(3+) chloride trihydrate was purchased from Alfa Aesar. 2,2-Bis(trifluoromethyl)oxirane is a DuPont product.

2-[(Di-*tert*-butylphosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol (1). A 10.0 g portion (0.0684 mol) of di-*tert*-butylphosphine, 12.93 g (0.0718 mol) of 2,2-bis(trifluoromethyl)oxirane, and 30 mL of THF were stirred at room temperature for 3 days. The solvent was evaporated under 1 mm vacuum. The residue was recrystallized from 40 mL of pentane at −30 °C. The yield of 2-[(di-*tert*-butylphosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol was 17.40 g (78%) as white crystals with mp 97.9 °C. Anal. Calcd for $C_{12}H_{21}F_6OP$ (mol wt 326.26): C, 44.18; H, 6.49; P, 9.49. Found: C, 44.34; H, 6.53; P, 9.73. ^1H NMR (500 MHz, C_6D_6, TMS): δ 0.97 (d, $^3J_{P,H}$ = 12.1 Hz, 18 H, Me), 2.11 (d, $^3J_{P,H}$ = 3.8 Hz, 2 H, P−CH_2), 9.10 (b, 1 H, OH). ^{19}F NMR (377 MHz, C_6D_6): δ −77.03 (d, $^4J_{PF}$ = 9.0 Hz). ^{31}P NMR (500 MHz, C_6D_6): δ 5.79 (sp, $^4J_{PF}$ = 9.0 Hz). The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 2.

2-(3,5-Bis(trifluoromethyl)phenyl)-4-methylpyridine (4). A 15.0 g portion (0.058 15 mol) of 3,5-bis(trifluoromethyl)-phenylboronic acid, 7.42 g (0.058 16 mol) of 2-chloro-4-methylpyridine, 17.43 g (0.1148 mol) of cesium fluoride, 0.53 g (0.000 579 mol) of tris(dibenzylideneacetone)dipalladium(0), 0.33 g (0.001 42 mol) of di-*tert*-butyl((trimethylsilyl)methyl)-phosphine, and 100 mL of 1,4-dioxane were stirred at room temperature for 12 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting mixture was purified by chromatography on silica gel with petroleum ether/ethyl ether (10/0.5) as eluent. The yield of 2-(3,5-bis-(trifluoromethyl)phenyl)-4-methylpyridine (**4**) was 16.18 g (91%) as a colorless liquid. ^1H NMR (500 MHz, $CDCl_3$): δ 2.56 (s, 3H, Me), 7.11 (s, 1H, arom H), 7.51 (s, 1H, arom H), 7.90 (s, 1H, arom H), 8.45−8.55 (m, 3H, arom H). ^{19}F NMR (377 MHz, $CDCl_3$): δ −63.35, −63.36 (1:1). Anal. Calcd for

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(13) Dura-Vila, V.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2000**, 1525.

(14) Lange, C. W.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 6582.

$C_{14}H_9F_6N$: C, 55.09; H, 2.97; N, 4.59. Found: C, 55.01; H, 3.12; N, 4.44.

Cyclometalation of 2-(3,5-Bis(trifluoromethyl)phenyl)-4-methylpyridine (4). A 3.80 g portion (0.0125 mol) of 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine (**4**), 4.20 g (0.0119 mol) of iridium(3+) chloride trihydrate, 20 mL of ethoxyethanol, and 2 mL of water were refluxed under argon with stirring for 12 h. The reaction mixture was cooled to room temperature, and 7.77 g (0.0238 mol) of 2-[(di-*tert*-butylphosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol (**1**) and 7.76 g (0.0238 mol) of cesium carbonate were added. The resulting reaction mixture was refluxed additionally for 60 h and purified by chromatography on silica gel with petroleum ether/ethyl ether (10/1) as eluent and then methanol at the end. The following compounds were isolated in order of elution from the column.

Iridium(II) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (2). The yield of **2** was 0.9 g as light blue crystals with mp 262.16 °C. ^{1}H NMR (500 MHz, THF[D_8], TMS): δ 1.20 (br, 1/2 of line width is 0.4 ppm, 36H, Me), 24.1 (br, 1/2 of line width is 0.3 ppm, 4 H, P−CH_2). ^{19}F NMR (377 MHz, THF[D8]): δ −58.05 (s, 12F, CF_3). Anal. Calcd for $C_{24}H_{40}F_{12}IrO_2P_2$ (mol wt 842.72): C, 34.21; H, 4.78; P, 7.35. Found: C, 34.09; H, 4.81; P, 7.49. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 2.

Hydridoiridium(III) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (3). The yield of **3** was 1.1 g as red crystals with mp 286.26 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ −47.8 (t, $^2J_{P,H}$ = 12.5 Hz, 1 H, H−Ir), 1.45 (br, 36 H, Me), 2.10 (br, 4 H, PCH_2). ^{19}F NMR (377 MHz, $CDCl_3$): δ −75.37 (q, $^4J_{FF}$ = 11.0 Hz), − 76.51 (q, $^4J_{FF}$ = 11.0 Hz). ^{31}P NMR (500 MHz, $CDCl_3$): δ 80.27 (d, $^2J_{P,H}$ = 12.5 Hz). Anal. Calcd for $C_{24}H_{41}F_{12}IrO_2P_2$ (mol wt 843.73): C, 34.16; H, 4.90; P, 7.34. Found: C, 34.10; H, 4.98; P, 7.44. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 2.

Dihydridoiridium(III) [3-(Di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*]-[2-[(di-*tert*-butyl-phosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol-κ*P*] (5). The yield of **5** was 1.4 g as golden crystals with mp 309.21 °C dec. ^{1}H NMR (500 MHz, C_6D_6): δ −30.61 (t, $^2J_{P,H}$ = 12.5 Hz, 2 H, H−Ir), 1.30 (br, 36 H, Me), 2.35 (br, 4 H, P−CH_2), 9.50 (br, 1 H, OH). ^{19}F NMR (377 MHz, C_6D_6): δ −75.54. ^{31}P NMR (500 MHz, C_6D_6): δ 79.70 (t, $^2J_{P,H}$ = 12.5 Hz). Anal. Calcd for $C_{24}H_{43}F_{12}IrO_2P_2$ (mol wt 845.74): C, 34.08; H, 5.12; P, 7.32. Found: C, 34.20; H, 5.15; P, 7.53. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 2.

Iridium(III) Carbonyl [3-(Di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*]-hydro[4,6-bis(trifluoromethyl)-2-(4-methyl-2-pyridinyl-κ*N*)phenyl-κ*C*] (6). The yield of **6** was 1.7 g as white crystals with mp 102.72 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ −16.38 (d, $^2J_{P,H}$ = 23.5 Hz, 1 H, H−Ir), 1.35 (d, $^3J_{P,H}$ = 12.1 Hz, 9 H, Me), 1.45 (d, $^3J_{P,H}$ = 12.1 Hz, 9 H, Me), 2.20 (br, 2H, CH_2P), 2.44 (s, 3 H, Me), 7.01 (s, 1 H, arom H), 7.60 (s, 1 H, arom H), 7.70 (s, 1 H, arom H), 8.15 (s, 1 H, arom H), 8.76 (s, 1 H, arom H). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −60.87 (br, 3 F), −63.14 (br, 3 F), −75.51 (br, 3 F), −76.58 (br, 3 F). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 74.02. Anal. Calcd for $C_{28}H_{31}F_{12}IrNO_2P$ (mol wt 864.72): C, 38.89; H, 3.61; P, 3.58. Found: C, 38.68; H, 3.60; P, 3.81. The structure was proved by X-ray analysis. A crystal suitable for X-ray analysis was grown from pentane. A summary of crystal data, data collection, and structural refinement parameters is given in Table 2.

Iridium(III) Bis[4,6-bis(trifluoromethyl)-2-(4-methyl-2-pyridinyl-κ*N*)phenyl-κ*C*] Chloride Adduct with Methanol and Diethyl Ether (7). The yield of **7** was 0.14 g as yellow crystals with mp 178.92 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.11 (t, $^3J_{H,H}$ = 8.0 Hz, 6 H, Me), 2.67 (s, 3 H, Me), 3.40 (q, $^3J_{H,H}$ = 8.0 Hz, 4 H, CH_2), 3.70 (b, 3H, MeO), 6.04−8.57 (m, 10 H, arom H). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −60.19 (br, 3 F), −63.25 (br, 3 F). Anal. Calcd for $C_{33}H_{30}ClF_{12}IrN_2O_2$ (mol wt 942.25): C, 42.06; H, 3.21; N, 2.97. Found: C, 42.12; H, 3.23; N, 3.07. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 3.

Hydridoiridium(III) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (3). Alternative Preparation Procedure. A 5.0 g portion (0.0329 mol) of lithium di-*tert*-butylphosphide, 6.51 g (0.0362 mol) of 2,2-bis(trifluoromethyl)oxirane, and 20 mL of THF were stirred at room temperature for 1 h. Then 5.2 g (0.0148 mol) of iridium(III) chloride trihydrate and 40 mL of isopropyl alcohol were added to the reaction mixture. The resulting slurry was refluxed under argon for 2 days. The red precipitate was collected by filtration, washed with 50 mL of cold isopropyl alcohol, and dried under 1 mm vacuum. The yield of **5** was 9.14 g (74%) as red crystals with spectroscopic data identical with those mentioned earlier.

Iridium(II) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (2). Alternative Preparation Procedure through Air Oxidation. A 0.5 g portion (0.000 59 mol) of hydridoiridium(III) *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (**3**) was dissolved in 500 mL of THF. A 0.001 g portion of tetraethylammonium hydroxide as a 40% solution in water, or an equimolar amount of 40% sodium hydroxide solution in water, was added into the reaction mixture. The mixture was exposed to air for 24 h, and then the solvent was removed under 1 mm vacuum and the residue was recrystallized from 20 mL of THF. The yield of compound **2** was 0.47 g (95%) as light blue crystals. The spectroscopic data were found to be identical with those mentioned earlier.

Iridium(II) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (2). Alternative Preparation Procedure through Sublimation. A 0.3 g portion (0.00036 mol) of hydridoiridium(III) *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (**3**) was placed in a sublimation tube (500 mm × 10 mm) and sublimated for 120 h at 1 mm and 190 °C. The yield of compound **2** was 0.18 g (59%) as light blue crystals. The spectroscopic data were found to be identical with those mentioned earlier.

Hydridoiridium(III) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] Carbonyl (9). A 0.5 g portion (0.000 59 mol) of hydridoiridium(III) *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (**3**) was dissolved in 30 mL of THF. Carbon monoxide was bubbled through this red solution until it became colorless (5−10 min). The reaction mixture was cooled to −35 °C. The resulting white precipitate was filtered and washed with 20 mL of pentane. The yield of **9** was 0.41 g (79%) as white crystals with mp 148.17 °C. ^{1}H NMR (500 MHz, THF[D_8]): δ −6.80 (t, $^2J_{P,H}$ = 15.0 Hz, 1 H, H−Ir), 0.45 (t, $^3J_{P,H}$ = 14.0 Hz, 18 H, Me), 0.65 (t, $^3J_{P,H}$ = 14.0 Hz, 18 H, Me), 2.20 (br, 4 H, PCH_2). ^{19}F NMR (377 MHz, THF[D_8]): δ −77.19 (q, $^4J_{FF}$ = 11.0 Hz), −77.94 (q, $^4J_{FF}$ = 11.0 Hz). ^{31}P NMR (500 MHz, THF[D_8]): δ 69.42 (d, $^2J_{P,H}$ = 12.5 Hz). Anal. Calcd for $C_{25}H_{41}F_{12}IrO_3P_2$ (mol wt 871.74): C, 34.44; H, 4.74; P, 7.11. Found: C, 34.29; H, 4.73; P, 7.08. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 3.

Hydridoiridium(III) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] 4-(1-Pyrrolidinyl)pyridine-κ*N*] (10). A 0.4 g portion (0.000 47 mol) of hydridoiridium(III) *trans*-bis[3-(di-*tert*-butyl-

Table 3. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters of 7 and 9−12

	7	**9**	**10**	**11**	**12**
empirical formula	$C_{33}H_{30}ClF_{12}IrN_2O_2$	$C_{25}H_{25}F_{12}IrO_3$	$C_{39}H_{65}F_{12}IrN_2O_{3.50}P_2$	$C_{25}H_{41}F_{12}IrO_3P_2$	$C_{24}H_{39}F_{12}IrO_2P_2$
fw	942.24	427.8	1100.07	871.72	841.69
cryst color, form	light, irreg block	colorless, wedge	colorless, rect plate	gold, irreg block	dark red, prism
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P1$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$
a (Å)	10.8837(15)	9.043(4)	22.181(8)	8.9000(8)	8.8560(9)
b (Å)	11.9141(16)	9.584(4)	19.728(7)	12.8523(12)	9.3124(9)
c (Å)	13.6025(18)	10.967(5)	21.614(7)	27.710(3)	11.1189(11)
α (deg)	100.636(3)	83.273(7)	90	90	65.715(2)
β (deg)	98.217(3)	70.193(7)	105.500(6)	91.7441(19)	75.941(2)
γ (deg)	94.766(3)	64.639(7)	90	90	65.218(2)
V (Å^3)	1704.8(4)	807.6(6)	9114(5)	3168.2(5)	756.11(13)
Z	2	2	8	4	1
density (g/cm^3)	1.836	1.759	1.603	1.828	1.849
abs μ (mm^{-1})	4.094	4.326	3.088	4.412	4.616
F(000)	920	414	4448	1720	414
cryst size (mm)	0.08 × 0.22 × 0.35	0.20 × 0.17 × 0.05	0.20 × 0.14 × 0.05	0.25 × 0.25 × 0.17	0.20 × 0.20 × 0.22
temp (°C)	−100	−100	−100	−100	−100
scan mode	ω	ω	ω	ω	ω
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.29	28.31	28.3	28.28	28.25
no. of obsd rflns	30 973	12 237	53 727	17 595	7494
no. of unique rflns	8195	3834	11 068	7368	3490
R_{merge}	0.0249	0.0365	0.1041	0.024	0.0491
no. of params	465	270	551	396	232
S^a	1.028	1.072	1.002	0.797	1.009
R indices ($I > 2\sigma(I)$)^b	wR2 = 0.0476	wR2 = 0.0858	wR2 = 0.1174	wR2 = 0.0502	wR2 = 0.0730
	R1 = 0.0190	R1 = 0.0389	R1 = 0.0546	R1 = 0.0235	R1 = 0.0395
R indices (all data)^b	wR2 = 0.0486	wR2 = 0.0900	wR2 = 0.1605	wR2 = 0.0562	wR2 = 0.0752
	R1 = 0.0205	R1 = 0.0493	R1 = 0.1450	R1=0.0325	R1 = 0.0440
max diff peak, hole (e/Å^3)	1.105, −0.871	0.944, −0.631	2.684, −0.911	1.691, −0.630	1.214, −0.801

[a] See footnote *a* in Table 2. [b] See footnote *b* in Table 2.

phosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] (**3**) was dissolved in 20 mL of THF. A 0.14 g portion (0.000 95 mol) of 4-pyrrolidin-1-ylpyridine was added to the reaction mixture. The reaction mixture was cooled to −35 °C. The resulting white precipitate was filtered and washed with 20 mL of pentane. The yield of **10** was 0.34 g (72%) as white crystals with mp 330.40 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ −24.0 (br, 1 H, H−Ir), 1.40 (t, $^3J_{P,H}$ = 13.4 Hz, 18 H, Me), 1.80 (t, $^3J_{P,H}$ = 13.4 Hz, 18 H, Me), 2.00 (br, 4 H, CH$_2$), 2.20 (br, 4 H, PCH$_2$), 3.60 (br, 4 H, NCH$_2$), 8.1 (br, 3 H, Py). ^{19}F NMR (377 MHz, THF[D$_8$]): δ −75.21 (br, 12F, CF$_3$). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 58.74. Anal. Calcd for $C_{33}H_{53}F_{12}IrN_2O_2P_2$ (mol wt 991.93): C, 39.96; H, 5.39; P, 6.25. Found: C, 40.05; H, 5.53; P, 6.31. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 3.

Reaction of Pyridine with Hydridoiridium(III) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] (3). A 0.4 g portion (0.00047 mol) of hydridoiridium(III) *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] (**3**) was dissolved in 20 mL of pyridine[D$_5$] upon heating. The resulting colorless solution was analyzed by ^{1}H, ^{19}F, and ^{31}P NMR measurements. ^{1}H NMR (500 MHz, Py[D$_5$]): δ −22.0 (br, 1 H, H−Ir), 2.60 (t, $^3J_{P,H}$ = 13.5 Hz, 18 H, Me), 3.00 (t, $^3J_{P,H}$ = 13.5 Hz, 18 H, Me), 3.50 (br, 2 H, PCH$_2$), 3.70 (br, 2 H, PCH$_2$), 8.7 (s, 2 H, Py), 8.8 (s, 1 H, Py), 9.1 (s, 1 H, Py). ^{19}F NMR (377 MHz, Py[D$_5$]): δ −72.99 (br, 6F, CF$_3$), −73.07 (br, 6F, CF$_3$). ^{31}P NMR (500 MHz, Py[D$_5$]): δ 62.74. The starting hydridoiridium(III) *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] (**3**) precipitates out from the reaction mixture upon standing at ambient conditions over a 2 week period.

Thermolysis of Complex 2. Iridium(III) *trans*-[3-(Di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] [[3-(*tert*-Butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*](3-(2-methylpropyl)-*κC*] (12). A solution of 2.86 g (0.003 39 mol) of complex **2** in 25 mL of trimethyl phosphate was kept at 110 °C in a 50 mL flask under argon for 12 h. When the reaction mixture was cooled to ambient temperature, red crystals of **12** precipitated. The yield of compound **12** was 1.34 g (47%) with mp 245.39 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ 0.93 (d, $^3J_{P,H}$ = 13.1 Hz, 3 H, Me), 1.07 (d, $^3J_{P,H}$ = 13.9 Hz, 9 H, Me), 1.13 (d, $^3J_{P,H}$ = 13.7 Hz, 9 H, Me), 1.22 (d, $^3J_{P,H}$ = 14.7 Hz, 9 H, Me), 1.40 (d, $^3J_{P,H}$ = 14.9 Hz, 3 H, Me), 2.10 (m, 4 H, CH$_2$), 3.54 (d,d,d, $^2J_{H,H}$ = 5.3 Hz, $^3J_{P,H}$ = 20.4 Hz, $^3J_{P,H}$ = 9.03 Hz. 1 H, Ir−CH$_2$), 3.80 (d, $^2J_{H,H}$ = 5.3 Hz, 1 H, Ir−CH$_2$). ^{19}F NMR (377 MHz, THF[D$_8$]): δ −77.60 (b, 6F), −78.43 (b, 6F), −79.40 (b, 12F). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 64.29 (d, $^2J_{P,P}$ = 356.5 Hz), 24.28 (d, $^2J_{P,P}$ = 356.5 Hz). A two-dimensional (^{1}H and ^{13}C) NMR experiment correlates the most upfield and characteristic peak of Ir−CH$_2$ δ −5.30 (d, $^2J_{P,C}$ = 23.0 Hz) in ^{13}C NMR with the two most downfield signals in ^{1}H NMR: δ 3.54 (d,d,d, $^2J_{H,H}$ = 5.3 Hz, $^3J_{P,H}$ = 20.4 Hz, $^3J_{P,H}$ = 9.03 Hz. 1 H, Ir−CH$_2$) and 3.80 (d, $^2J_{H,H}$ = 5.3 Hz, 1 H, Ir−CH$_2$). Anal. Calcd for $C_{24}H_{39}F_{12}IrO_2P_2$ (mol wt 841.71): C, 34.25; H, 4.67; P, 7.36. Found: C, 33.87; H, 4.31; P, 7.51. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 3.

Iridium(III) *trans*-[3-(Di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] [[3-(*tert*-Butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*](3-(2-methylpropyl)-*κC*] Carbonyl (13). A 0.5 g portion (0.000 59 mol) of iridium(III) *trans*-[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*] [[3-(*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-*κO*,*κP*](3-(2-methylpropyl)-*κC*] (**12**) was dissolved in 40 mL of THF. Carbon monoxide was bubbled through this red solution until it became colorless (5−10 min). The reaction mixture was cooled to −35 °C. The resulting white precipitate was filtered and washed with 30 mL of pentane. The yield of **13** was 0.48 g (93%) as white crystals with mp 235.17 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ 1.22 (d, $^3J_{P,H}$ = 15.6 Hz, 3 H, Me), 1.38 (d, $^3J_{P,H}$ = 13.8 Hz, 9 H, Me), 1.41 (d,

Table 4. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters of 13−16

	13	14	15	16
empirical formula	$C_{25}H_{39}F_{12}IrO_3P_2$	$C_{40}H_{60}F_{24}Ir_2O_{10}P_4$	$C_{16}H_{27}O_2P$	$C_{36}H_{60}IrO_4P_2$
fw	869.7	1665.16	282.35	810.98
cryst color, form	pink, irreg block	red, plate	colorless, irreg block	purple, prism
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	9.9034(8)	15.111(4)	8.1314(7)	12.3338(11)
b (Å)	11.1101(9)	12.496(4)	14.1976(12)	21.523(2)
c (Å)	15.6891(13)	15.398(4)	15.3965(14)	14.1769(13)
α (deg)	72.223(2)	90	96.420(2)	90
β (deg)	89.903(2)	98.374(5)	102.508(2)	97.324(2)
γ (deg)	73.369(2)	90	104.220(2)	90
V (Å^3)	1568.1(2)	2876.5(14)	1656.3(3)	3732.6(6)
Z	2	2	4	4
density (g/cm^3)	1.842	1.923	1.132	1.443
abs μ (mm^{-1})	4.457	4.86	0.163	3.697
F(000)	856	1620	616	1660
cryst size (mm)	0.23 × 0.22 × 0.14	0.02 × 0.08 × 0.32	0.40 × 0.24 × 0.08	0.25 × 0.08 × 0.05
temp (°C)	−100	−100	−100	−100
scan mode	ω	ω	ω	ω
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.29	28.29	28.31	33.17
no. of obsd rflns	27 023	23 029	26 975	117 107
no. of unique rflns	7538	6882	7880	14 213
R_{merge}	0.0362	0.0337	0.0296	0.0858
no. of params	397	369	359	497
S^a	1.048	1.053	1.007	1.154
R indices ($I > 2\sigma(I)$)^b	wR2 = 0.0908 R1 = 0.0350	wR2 = 0.0573 R1 = 0.0266	wR2 = 0.1025 R1 = 0.0407	wR2 = 0.1379 R1 = 0.0669
R indices (all data)^b	wR2 = 0.0959 R1 = 0.0418	wR2 = 0.0643 R1 = 0.0424	wR2 = 0.1191 R1 = 0.0632	wR2 = 0.1623 R1 = 0.1380
max diff peak, hole (e/Å^3)	3.566, −1.629	1.712, −0.779	0.330, −0.184	8.386, −1.808

[a] See footnote *a* in Table 2. [b] See footnote *b* in Table 2.

$^3J_{P,H}$ = 15.2 Hz, 9 H, Me), 1.50 (d, $^3J_{P,H}$ = 13.8 Hz, 9 H, Me), 1.63 (d, $^3J_{P,H}$ = 13.8 Hz, 3 H, Me), 2.1 (m, 2 H, Ir−CH$_2$), 2.50 (m, 4 H, CH$_2$). ^{19}F NMR (377 MHz, THF[D$_8$]): δ −77.49 (m, 3F, CF$_3$), −77.64 (m, 6F, CF$_3$), −79.30 (m, 3F, CF$_3$). ^{31}P NMR (500 MHz, THF[D$_8$]): δ −2.47 (d, $^2J_{P,P}$ = 323.0 Hz), 54.32 (d, $^2J_{P,P}$ = 323.0 Hz). A two-dimensional (^{1}H and ^{13}C) NMR experiment correlates the most upfield and characteristic peak of Ir−CH$_2$, δ 15.50 (d, $^2J_{P,C}$ = 30.9 Hz), in ^{13}C NMR with two multiplets at δ 2.1 (m, 2 H, Ir−CH$_2$) in ^{1}H NMR. Anal. Calcd for $C_{25}H_{39}F_{12}IrO_3P_2$ (mol wt 869.72): C, 34.52; H, 4.52; P, 7.12. Found: C, 34.73; H, 4.55; P, 7.40. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 4.

Oxidation of Iridium(III) *trans*-[3-(Di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] [[3-(*tert*-Butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*](3-(2-methylpropyl)-κ*C*]. Preparation of the Binuclear Cluster 14. A solution of 1.0 g (0.0012 mol) of complex **12** in 25 mL of trimethyl phosphate was kept at 110 °C in a 50 mL flask exposed to air for 12 h. The reaction mixture was purified by chromatography on silica gel with pentane/ethyl ether (10/1) as eluent. The yield of compound **14** as red crystals was 0.6 g (59%). Complex **14** was paramagnetic. NMR experiments gave unintelligible data. Anal. Calcd for $C_{40}H_{60}F_{24}Ir_2O_{10}P_4$ (mol wt 1665.19): C, 28.85; H, 3.63; P, 7.44. Found: C, 28.90; H, 3.71; P, 7.74. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 4.

Hydridoiridium(III) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (3). Alternative Preparation by Hydrogenation of Iridium(II) *trans*-Bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] (2). A solution of 0.15 g (0.000 18 mol) of complex **2** in 200 mL of THF was hydrogenated at 70 °C in an autoclave under 700 psi of total hydrogen pressure for 12 h. After the reaction mixture was cooled to ambient temperature, the solvent was removed under 1 mm vacuum. The residue was recrystallized from 10 mL of THF, affording red crystals of complex **3**. The yield of compound **3** was 0.11 g (73%). The spectroscopic data were found to be identical with those mentioned earlier.

Iridium(I) [3-(Di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κ*O*,κ*P*] [2-[(Di-*tert*-butyl-phosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol-κ*P*] Carbonyl (11). A 0.1 g portion (0.000 12 mol) of complex **2** was dissolved in 3 mL of THF. Carbon monoxide was bubbled through this blue solution until it became colorless (3−5 min). The reaction mixture was cooled to −35 °C. The resulting yellow crystals were filtered and analyzed. The yield of **11** was 0.064 g (62%) as yellow crystals with mp 177.95 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ 1.40 (d, $^3J_{P,H}$ = 14.2 Hz, 18 H, Me), 1.42 (d, $^3J_{P,H}$ = 13.7 Hz, 18 H, Me), 2.43 (d, $^2J_{P,H}$ = 10.7 Hz, 2 H, P−CH$_2$), 8.60 (s, 1 H, OH). ^{19}F NMR (377 MHz, THF[D$_8$]): δ −77.29 (m, 6F, CF$_3$), −79.10 (m, 6F, CF$_3$). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 50.42 (d, $^2J_{P,P}$ = 295.0 Hz), 85.44 (d, $^2J_{P,P}$ = 295.0 Hz). Anal. Calcd for $C_{25}H_{41}F_{12}IrO_3P_2$ (mol wt 871.74): C, 34.44; H, 4.74; P, 7.11. Found: C, 34.67; H, 4.84; P, 7.09. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 3.

Di-*tert*-Butyl-(2,6-dimethoxyphenyl)phosphine (15). A 22.94 g portion (0.165 mol) of 1,3-dimethoxybenzene and 0.3 mL of tetramethylethylendiamine were dissolved in 90 mL of diethyl ether. A 109 mL amount of 1.6 M butyllithium in hexane was added dropwise to the reaction mixture for a period of 20 min at 0 °C. The mixture was warmed to ambient temperature and stirred for 12 h. A 25.0 g amount (0.138 mol) of di-*tert*-butylchlorophosphine was added to the resulting white suspension, and the mixture was refluxed for 1 week. Then the reaction mixture was hydrolyzed with 200 mL of the degassed water, extracted with 200 mL of diethyl ether, and dried over magnesium sulfate. Fractional distillation under 0.1 mm vacuum afforded di-*tert*-butyl-(2,6-dimethoxyphenyl)-phosphine as a white solid with mp 53.53 °C. The yield of **15** was 11.20 g (28.67%). ^{1}H NMR (500 MHz, THF[D$_8$]): δ 1.42

(d, $^3J_{P,H} = 12.0$ Hz, 18 H, Me), 3.41 (s, 3 H, Me), 3.57 (s, 3 H, Me), 6.38 (d, $^3J_{H,H} = 8.0$ Hz, 1 H, Ph H), 6.47 (d,d, $^3J_{H,H} = 8.0$ Hz, $^4J_{P,H} = 6.5$, 1 H, Ph H), 7.20 (7, $^3J_{H,H} = 8.0$ Hz, 1 H, Ph H). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 20.36 (s, 1P). Anal. Calcd for $C_{16}H_{27}O_2P$ (mol wt 282.36): C, 68.06; H, 9.64; P, 10.97. Found: C, 68.12; H, 9.85; P, 11.17. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 4.

Hydridoiridium(III) *trans*-Bis[2-[bis(1,1-dimethylethyl)phosphino]-6-isopropyl-3-methoxyphenolato-*κO1,κP2*] (16). An 8.80 g portion (0.0312 mol) of di-*tert*-butyl(2,6-dimethoxyphenyl)phosphine (**15**), 5.00 g (0.0142 mol) of iridium(3+) chloride trihydrate, and 40 mL of 2-propanol were refluxed under argon with stirring for 66 h. The reaction mixture was cooled to room temperature. The precipitate was collected and recrystallized from 20 mL of methylene chloride. The yield of hydridoiridium(III) *trans*-bis[2-[bis(1,1-dimethylethyl)phosphino]-6-isopropyl-3-methoxyphenolato-*κO1,κP2*] (**16**) was 6.4 g (55.60%) as red crystals with mp 318.95 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ −47.9 (t, $^2J_{P,H} = 11.8$ Hz, 1 H, H−Ir), 1.05 (d, $^3J_{H,H} = 6.9$ Hz, 6 H, Me), 1.10 (d, $^3J_{H,H} = 6.9$ Hz, 6 H, Me), 1.38 (t, $^3J_{P,H} = 14.2$ Hz, 18 H, Me), 1.46 (t, $^3J_{P,H} = 14.9$ Hz, 18 H, Me), 3.44 (s, $^3J_{H,H} = 6.9$ Hz, 2 H, CHMe$_2$), 3.58 (s, 6H, Me), 5.95 (d, $^3J_{H,H} = 8.1$ Hz, 2 H, Ph H), 6.87 (d, $^3J_{H,H} = 8.1$ Hz, 2 H, Ph H). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 69.34 (d, $^2J_{P,H} = 11.8$ Hz). Anal. Calcd for $C_{36}H_{61}IrO_4P_2$ (mol wt 812.03): C, 53.25; H, 7.57; P, 7.63. Found: C, 53.29; H, 7.80; P, 7.56. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 4.

Hydridoiridium(III) *trans*-Bis[2-[bis(1,1-dimethylethyl)phosphino]-3-methoxyphenolato-*κO1,κP2*] (17). A 3.20 g portion (0.0113 mol) of di-*tert*-butyl(2,6-dimethoxyphenyl)phosphine (**15**), 1.00 g (0.002 84 mol) of iridium(3+) chloride trihydrate, and 20 mL of 2-propanol were refluxed under argon with stirring for 24 h. The reaction mixture was cooled to room temperature. The precipitate was collected and recrystallized from 10 mL of methylene chloride. The yield of hydridoiridium(III) *trans*-bis[2-[bis(1,1-dimethylethyl)phosphino]-3-methoxyphenolato-*κO1,κP2*] (**17**) was 0.34 g (16.50%) as red crystals with mp 281.60 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ −48.0 (t, $^2J_{P,H} = 11.9$ Hz, 1 H, H−Ir), 1.25 (t, $^3J_{P,H} = 14.3$ Hz, 18 H, Me), 1.34 (t, $^3J_{P,H} = 14.7$ Hz, 18 H, Me), 3.60 (s, 6 H, Me), 5.85 (m, 2 H, Ph H), 6.30 (d, $^3J_{H,H} = 8.1$ Hz, 2 H, Ph H), 6.85 (t, $^3J_{H,H} = 8.1$ Hz, 2 H, Ph H). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 70.00 (s, 1P). Anal. Calcd for $C_{30}H_{49}IrO_4P_2$ (mol wt 727.87): C, 49.50; H, 6.79; P, 8.51. Found: C, 49.70; H, 6.88; P, 8.51. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 5.

Iridium(III) *trans*-Bis[2-[bis(1,1-dimethylethyl)phosphino]-3-methoxyphenolato-*κO1,κP2*] (3-(2-Methylpropyl)-*κC*] (18). A 0.20 g portion (0.000 27 mol) of hydridoiridium(III) *trans*-bis[2-[bis(1,1-dimethylethyl)phosphino]-3-methoxyphenolato-*κO1,κP2*] (**17**) was dissolved in 20 mL of methylene chloride. The resulting solution was exposed to air for 12 h. The mixture was purified by chromatography on silica gel with petroleum ether/ethyl ether (10/0.5) as eluent. Two compounds were isolated. The yield of compound **18** was 0.09 g (50%) with mp 229.90 °C. ^{1}H NMR (500 MHz, THF[D$_8$]): δ 0.79 (d, $^3J_{P,H} = 13.8$ Hz, 3 H, Me), 1.15 (d, $^3J_{P,H} = 13.8$ Hz, 9 H, Me), 1.37 (d, $^3J_{P,H} = 14.7$ Hz, 9 H, Me), 1.52 (d, $^3J_{P,H} = 14.4$ Hz, 9 H, Me), 1.68 (d, $^3J_{P,H} = 14.9$ Hz, 3 H, Me), 3.54 (d,d,d, $^2J_{H,H} = 5.6$ Hz, $^3J_{P,H} = 22.7$ Hz, $^3J_{P,H} = 10.02$ Hz. 1 H, Ir−CH$_2$), 3.05 (s, $^2J_{H,H} = 5.6$ Hz, 1 H, Ir−CH$_2$), 3.55 (s, 3H, Me), 3.76 (d, $^4J_{P,H} = 7.7$ Hz, 3 H, Me), 5.98 (m, 2H, Ph H), 6.50 (m, 2H, Ph H), 6.95, (m, 2H, Ph H). ^{31}P NMR (500 MHz, THF[D$_8$]): δ 54.66 (d, $^2J_{P,P} = 329.2$ Hz), 19.33 (d, $^2J_{P,P} = 329.2$ Hz). Anal. Calcd for $C_{30}H_{47}IrO_4P_2$ (mol wt 725.86): C, 49.64; H, 6.53; P, 8.53. Found: C, 50.11; H, 6.58; P, 8.26.

Table 5. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters of 17, 19, and 20

	17	**19**	**20**
empirical formula	$C_{30}H_{49}IrO_4P_2$	$C_{30}H_{47}ClIrO_4P_2$	$C_{36},H_{58}IrO_6P_2$
fw	727.83	761.27	420.48
cryst color, form	red, rect plate	black, rect prism	black, rhombus
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	8.1966(8)	9.7988(11)	9.0060(10)
b (Å)	8.6598(9)	12.3642(14)	12.0664(13)
c (Å)	12.0745(12)	26.219(3)	17.0127(19)
α (deg)	78.0812(16)	90	90
β (deg)	88.8327(17)	94.735(2)	100.517(2)
γ (deg)	69.7442(15)	90	90
V (Å^3)	785.50(14)	3165.7(6)	1817.7(3)
Z	1	4	4
density (g/cm^3)	1.539	1.597	1.536
abs μ (mm^{-1})	4.383	4.435	3.803
F(000)	368	1532	858
cryst size (mm)	0.24 × 0.20 × 0.04	0.20 × 0.13 × 0.05	0.24 × 0.24 × 0.24
temp (°C)	−100	−100	−100
scan mode	ω	ω	ω
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.27	28.29	28.32
no. of obsd rflns	12 248	17 253	26 785
no. of unique rflns	3722	7426	4383
R_{merge}	0.0332	0.0408	0.0296
no. of params	207	356	213
S^a	1.052	1.07	1.1
R indices ($I > 2\sigma(I)$)^b	wR2 = 0.0671 R1 = 0.0300	wR2 = 0.0688 R1 = 0.0384	wR2 = 0.0464 R1 = 0.0199
R indices (all data)^b	wR2 = 0.0694 R1 = 0.0334	wR2 = 0.0787 R1 = 0.0715	wR2 = 0.0553 R1 = 0.0371
max diff peak, hole (e/Å^3)	0.893, −0.786	1.299, −0.846	1.277, −0.378

[a] See footnote *a* in Table 2. [b] See footnote *b* in Table 2.

Iridium(IV) *trans*-Bis[2-[bis(1,1-dimethylethyl)phosphino]-3-methoxyphenolato-*κO1,κP2*] (3-(2-Methylpropyl)-*κC*] Chloride (19). The yield of iridium(IV) *trans*-bis[2-[bis(1,1-dimethylethyl)phosphino]-3-methoxyphenolato-*κO1,κP2*] (3-(2-methylpropyl)-*κC*] chloride (**19**) was 0.04 g (19.0%) as dark blue crystals with mp 232.56 °C. The complex is paramagnetic. The powder spectrum shows a very large **g**-tensor anisotropy along three molecular axes and three distinct principal values of the **g** tensor ($g_1 = 2.49$, $g_2 = 2.38$, $g_3 = 2.23$) having observable hyperfine interactions with only one ^{31}P nucleus along one molecular axis. Anal. Calcd for $C_{30}H_{47}ClIrO_4P_2$ (mol wt 761.31): C, 47.33; H, 6.22; P, 8.14. Found: C, 47.39; H, 6.25; P, 8.20. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 5.

Iridium(IV) *trans*-Bis[2-[(1,1-dimethylethyl)phosphino]-[2-methyl-1-propanolato-*κO*]-3-methoxyphenolato-*κO1,κP2*] (20). A 0.4 g portion (0.000 49 mol) of hydridoiridium(III) *trans*-bis[2-[bis(1,1-dimethylethyl)phosphino]-6-isopropyl-3-methoxyphenolato-*κO1,κP2*] (**16**) was dissolved in 400 mL of THF. A 0.1 g portion of 40% sodium hydroxide solution in water was added to the reaction mixture. The mixture was exposed to air for 24 h, and then the solvent was removed under 1 mm vacuum and the residue was purified by chromatography on silica gel with petroleum ether/ethyl ether (10/0.5) as eluent. The yield of the iridium(IV) species **20** was 0.11 g (26.8%) as dark blue crystals with mp 251.31 °C. The complex **16** is paramagnetic. The powder spectra shows a very large **g**-tensor anisotropy along three molecular axes and three distinct principal values of the **g** tensor ($g_1 = 2.49$, $g_2 = 2.24$, $g_3 = 1.77$); a weak hyperfine interaction with one ^{31}P nucleus is observed along two principal directions (30 and 25 G), whereas hyperfine interactions with both ^{31}P nuclei are observed along the third direction (113 G, 50 G). Anal. Calcd for $C_{36}H_{58}IrO_6P_2$ (mol wt 841.01): C, 51.41; H, 6.95; P, 7.37.

Found: C, 51.60; H, 7.03; P, 7.22. The structure was proved by X-ray analysis. A summary of crystal data, data collection, and structural refinement parameters is given in Table 5.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **1**−**3**, **5**−**7**, **9**−**17**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary crystallographic data for this paper can also be obtained from the CCDC. The data for these 17 X-ray structures can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; deposit@ccdc.cam.ac.uk). The deposition numbers are CCDC 241281−241297 for compounds **1**−**3**, **5**−**7**, **9**−**17**, **19**, and **20**, respectively.

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