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Formation and Site-Selective Reactivity of a Nonsymmetric Dinuclear Iridium BisMETAMORPhos Complex

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Supporting Information

ABSTRACT: A flexible di(sulfonamidophosphine) ligand (**1**^{H2}, Ph₂PN^HS(O)₂N^HPPh₂) was synthesized from commercially available sulfamide and chlorodiphenylphosphine. Coordination of this new bisMETAMORPhos **1**^{H2} with [Ir(Cp*)Cl(μ-Cl)]₂ instantly led to the formation of the P,P-coordinated bimetallic complex **2** [Ir(Cp*)Cl(κ¹-P₁; κ¹-P₂-**1**^{H2})Ir(Cp*)Cl]. Reaction of **2** using excess NaOAc led to the formation of nonsymmetric homodinuclear complex **3** [Ir(Cp*)Cl(κ²-P,O; κ³-P,N,C; μ-1)Ir(Cp*)], which contains two distinctly different Ir^{III} centers, with a *fac*-P,N,C and a *fac*-P,O,Cl coordination environment. The ligand is overall trisanionic due to additional intramolecular C–H activation of a flanking phenyl ring. Complex **3** reacts selectively at the Ir(P,O,Cl) center with a single equivalent of HCl or H₂ to generate complexes **4** and **5**, respectively. These complexes are generated via heterolytic cleavage of the H–Cl or H–H bond, which reprotonates the ligand showing its bifunctional applicability. The Ir–C bond is found to be inert under these conditions.

INTRODUCTION

The construction of systems containing two metal centers using dinucleating ligands is well-established in coordination chemistry.^{1,2} Symmetric homodinuclear complexes preclude site-selective reactivity, while heterobimetallic species may require more tedious synthetic protocols. Homodinuclear complexes that feature two identical metal ions in the same oxidation state but in nonidentical coordination geometries are interesting targets, because the two metal centers can be expected to display nonequivalent chemical reactivity, due to their different coordination environment. Ditopical ligand scaffolds typically require divergent synthetic protocols. Individually addressable reactive ligand sites obtained from a chemical reaction of an initially symmetric backbone could result in nonequivalency of two identical metal ions without the need for complex backbone synthesis, see Figure 1. There is currently much interest in the development of chemo-responsive ligands that can participate in bond activation processes. However, predominantly mononuclear complexes are targeted to date, whereas integration of ligand reactivity into dinuclear architectures is less explored.³ To ensure potential communication between two metal centers, these ligand reactive sites should be in close proximity, while maintaining the opportunity for selective reactivity of individual ligand sites.

We have recently designed sulfonamidophosphine (METAMORPhos, PN^HS(O)₂) ligands that exhibit proton-responsive and hydrogen bonding properties and that can accommodate two metal ions with bridging P–N units.^{4,5} We also described

Figure 1. Preparation of a nonsymmetric homodinuclear iridium complex: (i) initial symmetric coordination of two metals to the ligand binding sites (L); (ii) selective ligand-based reactivity to create two nonequivalent binding sites (L and L*).

mononuclear iridium complexes with bisMETAMORPhos ligands, bearing a rigid xanthene backbone, that acted as tetradentate ligand to Ir^I and Ir^{III}.⁶ Herein we detail the preparation of a more flexible bisMETAMORPhos ligand, **1**^{H2}, based on an all-inorganic backbone, that is conveniently prepared in a single step from readily available starting materials. The two reactive –N^HP units are separated only by a tetrahedral S(O)₂ pivot. Next, the coordination of this symmetric ligand scaffold to [Ir(Cp*)Cl(μ-Cl)]₂ is described. The wealth of chemistry developed with IrCp* complexes led us to choose this as proof-of-concept starting point.⁷ Most notably, the intrinsic chemical reactivity embedded in this

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flexible bisMETAMORPhos ligand framework allowed the preparation of an Ir^{III}-dimer with two dissimilar iridium centers. As a result, heterolytic activation of H₂, which is relevant in the context of metal–ligand bifunctional bond activation,⁸ can be carried out selectively at one of the Ir centers, leaving the second Ir^{III} center intact.

RESULTS AND DISCUSSION

BisMETAMORPhos ligand **1**^{H2} (Ph₂PNHS(O)₂NHPPh₂) was obtained via a condensation reaction of 2 equiv of chlorodiphenylphosphine with 1 equiv of sulfamide in toluene and triethylamine as a base (Scheme 1). Typically, META-

Scheme 1. Synthesis of bisMETAMORPhos Ligand **1**^{H2} with Its Two Tautomeric Forms (P^{III}–P^{III} and P^{III}–P^V), Observed in a 1:0.9 Ratio in CD₂Cl₂

MORPhos ligands are prepared in THF. However, when THF was used as solvent for the preparation of **1**^{H2}, a mixture of mono- and bis(imino-bisphosphine) (Ph₂P–PPh₂==NS(O)₂)^{4b,c} and mono- and bisMETAMORPhos compounds was obtained, which are all in equilibrium. In toluene, **1**^{H2} coprecipitates with triethylammonium chloride (NEt₃·HCl) as a white powder, which drives the reaction to full conversion. In dichloromethane, **1**^{H2} exists as a mixture of two tautomers, the P^{III}–P^{III} state (**1**^{H2a}) and the P^{III}–P^V state (**1**^{H2b}) in roughly a 1:1 ratio. These tautomers can easily be distinguished by ³¹P NMR spectroscopy, because **1**^{H2a} displays a broad singlet at 33.5 ppm while tautomer **1**^{H2b} gives a broad singlet at 29.6 ppm and a broad doublet at 6.2 ppm (*J*_{P–H} 482 Hz) in CD₂Cl₂. The P^V–P^V tautomer of **1**^{H2} was not observed.

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a CH₂Cl₂ solution; see Figure 2 for the molecular structure of **1**^{H2}. The P₁–N₁

Figure 2. Molecular structure of **1**^{H2} obtained by X-ray diffraction. Selected bond lengths in Å: P₁–N₁ 1.7083(19), N₁–S₁ 1.6155(19), S₁–O₁ 1.4241(18).

(1.7083(19) Å), N₁–S₁ (1.6155(19) Å), and S₁–O₁ (1.4241(18) Å) bond lengths indicate that the solid state structure corresponds to tautomer **1**^{H2a}. Both nitrogen atoms in the molecular structure were found to be unusually flat, likely due to an intermolecular N–H⋯P interaction, with an N–P distance of 3.517(2) Å and an (N)H–P distance of 2.702(19) Å (see Supporting Information for the difference Fourier map).

Mixing 1 equiv of **1**^{H2} and 1 equiv of iridium precursor [Ir(Cp^{*})Cl(μ-Cl)]₂ in CH₂Cl₂ instantly led to the clean formation of a single species (**2**), according to NMR spectroscopic analysis. Complex **2** possesses a high degree of symmetry, as a sharp singlet was observed at 41.1 ppm in the ³¹P{¹H} NMR spectrum. In the corresponding ¹H NMR spectrum, the NH of the ligand is observed as a doublet at 6.8 ppm (²*J*_{H–P} = 10.9 Hz), which is shifted downfield by 1.3 ppm compared with the free ligand. On the basis of these observations as well as HR-MS data, species **2** was formulated as a symmetric dinuclear P,P-coordinated complex IrCl₂(Cp^{*})-(κ¹-P₁;κ¹-P₂-**1**^{H2}) (Scheme 2).

Scheme 2. Coordination of Ligand **1**^{H2} and [Ir(Cp^{*})Cl(μ-Cl)]₂ To Form Complex **2**

When **2** was stirred at room temperature in CH₂Cl₂ with excess NaOAc, in an attempt to deprotonate both –NH groups of the ligand and potentially generate different (e.g., P,O and P,N) coordination pockets, clean conversion to a new species (**3**) was observed. The ³¹P{¹H} NMR spectrum indicates the presence of two nonequivalent phosphorus nuclei, as two doublets at 73.3 and 19.9 ppm (*J*_{P–P} of 4 Hz) were observed. The ¹H NMR spectrum contains four distinctive phenyl rings and two different Cp^{*}-fragments, suggesting a highly non-fluxional structure that persists at elevated temperature (60 °C). Interestingly, integration of the signals in the aromatic region showed the loss of one aromatic proton. Complex **3** is therefore suggested to be the product of an intramolecular C–H activation of one of the phenyl rings of the ligand, with overall formulation of this species as [Ir(Cp^{*})Cl(κ²-P₁O;κ³-P₂N,C-1)(Ir(Cp^{*}))]. Analysis by mass spectrometry confirms this hypothesis (*m/z* for C₄₄H₄₉ClIr₂N₂O₂P₂S, 1150.20248). The structure was unequivocally confirmed by X-ray diffraction of single crystals, obtained by slow diffusion of pentane into a CH₂Cl₂ solution of **3**. The molecular structure (see Figure 3) shows that indeed an intramolecular C–H activation of one of the phenyl rings at phosphorus has occurred.⁹ As a result, a highly unusual, constrained, and nonsymmetric geometry for the completely inorganic ligand backbone was obtained. The two iridium centers in **3** have different coordination environments (apart from the Cp^{*} ligand) with a P,N,C and a P,O,Cl coordination sphere. The flexible bisMETAMORPhos ligand acts as both a bidentate (P₂₁,O for Ir₁) and a tridentate (P₁₁,N,C for Ir₂) ligand. The involvement of the sulfone oxygen in metal coordination was previously observed for other METAMORPhos ligands, but coordination of the sulfonamide nitrogen atom is unprecedented. The nitrogen N₂₁ is the central element of *three* different five-membered ring structures. The nonactivated phenyl ring **D** of P₂₁ is fixed between the two cyclopentadiene ligands (Cp^{*} and Cp^{*}'), and both Cp^{*} fragments are in close proximity to the phenyl ring (3.162(12) Å and 3.272(13) Å based on shortest C⋯C distances of the major disorder components). As a result, phenyl ring **D** is locked in position and cannot rotate freely, which is in agreement with the ¹H NMR spectral data. The ligand

Figure 3. Crystal structure obtained by X-ray diffraction and schematic presentation of **3**. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Only the major disorder components of Cp^* at Ir_2 and of the noncoordinated phenyl at P_{21} are shown. Selected bond lengths in Å: $\text{Ir}_1\text{--Cl}_1$ 2.3801(13), $\text{Ir}_1\text{--P}_{21}$ 2.2939(14), $\text{Ir}_1\text{--O}_{21}$ 2.155(3), $\text{P}_{21}\text{--N}_{21}$ 1.671(4), $\text{N}_{21}\text{--S}_1$ 1.643(4), $\text{S}_1\text{--O}_{21}$ 1.493(3), $\text{S}_1\text{--O}_{11}$ 1.447(4), $\text{S}_1\text{--N}_{11}$ 1.560(4), $\text{N}_{11}\text{--P}_{11}$ 1.649(4), $\text{Ir}_2\text{--P}_{11}$ 2.2918(13), $\text{Ir}_2\text{--C}_{241}$ 2.059(5). Selected angles (deg): $\text{P}_{11}\text{--Ir}_2\text{--N}_{21}$ 81.50(12), $\text{N}_{21}\text{--Ir}_2\text{--C}_{241}$ 82.30(19), $\text{P}_{21}\text{--Ir}_1\text{--O}_{21}$ 79.73(9).

backbone contains both a sulfamide $\text{S}\text{--N}$ ($\text{N}_{21}\text{--S}_1$ 1.643(4) Å) and a sulfimine $\text{S}\text{=N}$ bond ($\text{S}_1\text{--N}_{11}$ 1.560(4) Å). Correspondingly, a single bond between $\text{S}_1\text{--O}_{21}$ of 1.493(3) Å exists, while the $\text{S}_1\text{--O}_{11}$ bond is significantly shorter at 1.447(4) Å, indicating $\text{S}\text{=O}$ character. The iridium–carbon bond length ($\text{Ir}_2\text{--C}_{241}$) of 2.059(5) Å is in the range for previously reported $\text{Ir}\text{--C}_{\text{aryl}}$ bonds.¹⁰ In agreement with the retention of an $\text{Ir}\text{--C}$ bond in solution, C_{241} appears as a doublet-of-doublets at 153.2 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, with coupling to both phosphorus nuclei ($^2J_{\text{C-P}}$ 14.2 and 13.6 Hz).¹⁰ Two-dimensional NMR studies ($^1\text{H}\text{--}^{31}\text{P}$ NOESY and $^1\text{H}\text{--}^1\text{H}$ COSY) were performed to further elucidate the ^{31}P and ^1H NMR spectra of complex **3** (see Figures S1 and S2 in the Supporting Information).

The formation of **3** is proposed to occur via initial formation of **3'** formed through double dehydrohalogenation of the iridium centers and the ligand --NH groups (Scheme 3) with 2 equiv of NaOAc. Complex **3'** subsequently undergoes intramolecular $\text{C}\text{--H}$ bond activation at the *ortho*-position of a suitably positioned phenyl group (**C**) followed by dehydrohalogenation. This process may be assisted by NaOAc, a well-known base for intramolecular $\text{C}\text{--H}$ activation.¹⁰ An alternative pathway involving deprotonation of one --NH group and $\text{C}_{\text{sp}^2}\text{--H}$ activation is deemed less likely, but this possibility cannot be excluded to date. Attempts to isolate **3'** by applying 2 equiv of NaOAc led to the incomplete conversion of **2** into **3** at room temperature.¹¹ Applying different bases such as NEt_3 or DBU for the deprotonation of **2** also led to the formation of **3**, although with lower conversions, longer reaction times, and lower chemoselectivity.

The presence of two different iridium centers stimulated us to investigate the difference in reactivity in the two metal centers. Reaction of complex **3** with 1 equiv of HCl led to an

Scheme 3. Proposed Two-Step Pathway for the Formation of Complex **3** via Sequential Deprotonation of Complex **2**^a

^aInitial deprotonation of both --NH groups results in species **3'**, which undergoes facile intramolecular $\text{C}\text{--H}$ activation to yield complex **3**.

instantaneous color change from orange to yellow. The $\text{Ir}\text{--PNC}$ center remained intact, as deduced from ^1H , ^{31}P , and ^{13}C NMR spectroscopic data, which suggests selective reactivity at the $\text{Ir}(\text{P},\text{O},\text{Cl})$ center to give product **4** (Scheme 4) with

Scheme 4. Reversible Protonation of Complex **3** with HCl To Give Complex **4**

reprotonation of the sulfimine nitrogen. The transformation of complex **3** to **4** is fully reversible, as addition of NaOAc cleanly regenerates **3**. Treating **4** with an excess of HCl (2–10 equiv) did not lead to further reactivity (e.g., rupture of the $\text{Ir}\text{--C}$ or $\text{Ir}\text{--N}$ bond in **4**). In the ^1H NMR spectrum, the $\text{N}\text{--H}$ signal of **4** was found to be particularly broad and shifted downfield (9.3 ppm), which might indicate a hydrogen bonding interaction. This was supported by a DFT optimized structure of **4** (BP86, def2-TZVP) (Figure 4; red dotted line, $\text{H}\cdots\text{Cl}$ distance of 2.125 Å). The analogous complex with protonation occurring at the sulfone oxygen to give an --OH fragment (**4'**, see Supporting

Figure 4. DFT (BP86, def2-TZVP) optimized structure for **4**, displaying an intramolecular $\text{N}\text{--H}\cdots\text{Cl}$ interaction with an $\text{H}\cdots\text{Cl}$ distance of 2.125 Å.

Information) was calculated to be significantly higher in energy than **4** (ΔG_{298K}° 10.5 kcal mol⁻¹).

Heterolytic cleavage of H₂ at a mononuclear Ru(κ^2 -P,O-METAMORPhos) piano-stool complex in THF was previously reported by our group.^{4b} Complex **3** also shows selective reactivity toward dihydrogen at only the Ir(P,O,Cl) center (Scheme 5), according to in situ multinuclear NMR spectroscopy.

Scheme 5. Heterolytic Cleavage of H₂ by Complex **3 Generating Monohydride Complex **5**, via Initially Formed OH-Intermediate **5'****

copy. However, it was necessary to use a mixture of THF-*d*₈/CD₂Cl₂ (2:1), because **3** does not dissolve in neat THF. Under 5 bar of H₂ and at room temperature, a minor signal corresponding to an Ir-hydride was observed in ¹H NMR spectroscopy after 2 h. Heating the reaction mixture to 50 °C for a period of 20 h resulted in the clean conversion to complex **5**. Two singlets were observed in the ³¹P{¹H} NMR spectrum at 67.7 and 28.6 ppm. The former signal converts to a doublet (²J_{P-H} 32.3 Hz) in the proton-coupled ³¹P NMR spectrum. A single hydride signal (one H) was observed as a doublet at -15.5 ppm (*J*_{P-H} 35.1 Hz) in the ¹H NMR spectrum. The N-H resonance of **5** at 7.7 ppm (*J*_{H-P} = 2.0 Hz) in the ¹H NMR spectrum is strongly upfield shifted compared with that of complex **4**, which can be explained by the stronger N-H...Cl interactions relative to N-H...H interactions.¹² Complex **5** proved highly unstable and oxygen-sensitive upon release of dihydrogen pressure.

When the reaction was performed in pure CD₂Cl₂, no formation of **5** is observed even after 20 h at room temperature. Likely, a more polar solvent such as THF facilitates decoordination of the chloride to generate a vacant site, which enables the addition of H₂ over the Ir-O bond forming intermediate **5'** (potentially via an initial Ir-H₂ adduct). This observation also explains the "sluggish" reaction conditions of 20 h when using a 2:1 THF-*d*₈/CD₂Cl₂ mixture. Species **5'** rearranges to **5** via an OH-to-NH proton shuttle and chloride recoordination, see Scheme 5. In line with the speculated solvent dependence of this reaction with H₂, it was observed that initial reaction of **3** with 1 equiv of NaBAR^F in CD₂Cl₂, to induce Cl abstraction and formation of a corresponding cationic Ir₂ species, with subsequent addition of H₂ at room temperature, instantaneously afforded the analogous cationic Ir-hydride complex, according to high pressure *in situ* NMR analysis. The Ir₂-C₂₄₁ bond in **3** and **5** proved to be completely unreactive under an atmosphere of H₂.

CONCLUSIONS

The flexible bisMETAMORPhos ligand **1**^{H2}, which is conveniently prepared from commercially available sulfamide, allows for the formation of both symmetric and nonsymmetric homodinuclear Ir^{III}₂-complexes. Bis-phosphine P,P-coordinated complex **2** was obtained after reaction of **1**^{H2} with [Ir(Cp*)(Cl)(μ-Cl)]₂. Upon attempting to deprotonate the N-H groups of this bisMETAMORPhos ligand in dinuclear iridium complex **2** with NaOAc, unexpected intramolecular C-H activation of a phenyl ring of the ligand was observed, resulting in the selective formation of complex **3**. Interestingly, complex **3** contains two iridium centers with distinctly different coordination environments (P,N,C and P,O,Cl). Complex **3** reacts cleanly and selectively at the Ir-P,O,Cl center with a single equivalent of HCl or H₂ to give complexes **4** and **5**, respectively. These complexes are generated via heterolytic cleavage of the H-Cl or H-H bond, which reprotonates one of the nitrogens of the ligand, confirming the bifunctional applicability of the ligand. Complex **4** contains an N-H...Cl-Ir hydrogen bond interaction resulting from the proximity of the N-H functionality to the metal center, which can be important for potential cooperative reactivity. Further investigations into the reactivity of **3** are currently being performed in order to investigate whether the Ir-P,N,C center is also susceptible to exchange reactions (likely involving Ir-C bond rupture) and to employ complexes **4** and **5** for follow-up (catalytic) reactivity.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in dry glassware under nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. THF, toluene, and pentane were distilled from sodium under dinitrogen; CH₂Cl₂ and diethyl ether were collected from an MBraun SPS-800 system. Deuterated solvents were degassed by four freeze-pump-thaw cycles and dried over molecular sieves (4 Å). NMR spectra were measured on a Bruker AMX 400 (¹H, 400.1 MHz; ¹³C, 100.6 MHz; and ³¹P, 162.0 MHz) or on a Varian Mercury 300 (¹H, 300.1 MHz) spectrometer. High resolution mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV mass spectrometer.

Materials. Triethylamine (Sigma-Aldrich) was freshly distilled from CaH₂ and stored over molecular sieves (4 Å) prior to use. Chlorodiphenylphosphine (Sigma-Aldrich) was freshly distilled prior to use. All other reagents were purchased from commercial suppliers and used without further purification: sulfamide (Maybridge), [Cp*IrCl₂]₂ (Strem Chemicals).

Synthesis of **1^{H2}.** Sulfamide (1.15 g, 12 mmol) was added to a solution of triethylamine (2.5 equiv) in toluene (60 mL) and stirred at room temperature. Chlorodiphenylphosphine (4.3 mL, 24 mmol) was added dropwise, and the reaction mixture was stirred for 24 h at room temperature, leading to the precipitation of the ligand and triethylammonium chloride. The formed precipitate was filtered, and the residue washed with cold toluene (3 × 10 mL). The residue was then submitted to hot THF (4 × 10 mL) to dissolve the product. The organic phase was collected and concentrated to give **1** as a white pure solid in 70% yield (3.9 g). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, ratio **1a**/**1b** 1.13/1) δ 33.46 (s), 29.56 (d, ⁴J_{PP} = 10.3 Hz), 6.20 (d, ⁴J_{PP} = 10.2 Hz); ³¹P NMR (162 MHz, CD₂Cl₂, ratio **1a**/**1b** 1.13/1) δ 33.46 (br. s), 29.56 (br. s), 6.19 (br. d, ¹J_{PH} approximately 482 Hz); ¹H NMR (400 MHz, CDCl₃, integration based on minor isomer **1b**) δ 8.15 (d, ¹J_{PH} = 482.1 Hz, 1H, PH), 7.67 (dd, ³J_{PH} = 14.6, ³J_{HH} = 7.1 Hz, 4H), 7.60 (dd, ³J_{HH} = 8.3, ⁵J_{HP} = 6.6 Hz, 2H), 7.46 (td, ³J_{HH} = 7.7, ⁴J_{PH} = 3.4 Hz, 4H), 7.42–7.27 (m, 32.6H), 5.54 (d, ²J_{PH} = 5.5 Hz, 2.2H, NH), 5.39 (d, ³J_{PH} = 7.2 Hz, 1H, NH); ¹H{³¹P} NMR (400 MHz, CD₂Cl₂, integration based on minor isomer **1b**) δ 8.15 (s, 1H, PH), 7.67 (d, ³J_{HH} = 7.3 Hz, 4H), 7.60 (t, ³J_{HH} = 8.3 Hz, 2H), 7.46 (t,

$^3J_{\text{HH}} = 7.7$ Hz, 4H), 7.41–7.29 (m, 32.6H), 5.54 (s, 2.2H, NH), 5.39 (s, 1H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 138.02 (d, $^1J_{\text{PC}} = 8.9$ Hz, C_{quat}), 131.87 (s, CH), 131.77 (s, CH), 131.65 (s, CH), 130.11 (s, CH), 129.02 (s, CH). HR MS (FD^+): m/z calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2\text{P}_2\text{S}_1 [\text{M}]^+$ 464.08772, observed 464.08721.

Synthesis of 2. Ligand **1** (116 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (5 mL) together with $[\text{Ir}(\text{Cp}^*)\text{Cl}(\mu\text{-Cl})]_2$ (199 mg, 0.25 mmol) and stirred at room temperature for 1 h. The reaction mixture was concentrated to approximately 0.5, and 10 mL pentane was added. The orange suspension that formed was stirred for 1 h and filtered. The orange residue was collected and submitted to vacuum. Complex **2** was isolated as an orange powder (yield 92%). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 41.17 (s); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.95–7.89 (m, 8H), 7.51–7.46 (m, 12H), 6.79 (d, $^3J_{\text{PH}} = 10.9$ Hz, 2H), 1.29 (d, $^4J_{\text{PH}} = 2.4$ Hz, 30H); $^1\text{H}\{^{31}\text{P}\}$ NMR (400 MHz, CD_2Cl_2) δ 7.95–7.89 (m, 8H), 7.51–7.46 (m, 12H), 6.79 (s, 2H), 1.29 (s, 30H). HR MS (ESI^+): m/z calcd For $\text{C}_{44}\text{H}_{52}\text{Cl}_4\text{Ir}_2\text{N}_2\text{O}_2\text{P}_2\text{S}$ $[\text{M}]^+$ 1260.1237, observed 1260.1203.

Synthesis of 3. Ligand **1** (116 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (5 mL) together with $[\text{Ir}(\text{Cp}^*)\text{Cl}(\mu\text{-Cl})]_2$ (199 mg, 0.25 mmol) and stirred at room temperature for 1 h. To the orange reaction mixture was added 10 equiv of NaOAc (205 mg, 2.5 mmol), and the suspension was stirred for 16 h. In time, a color change from deep orange to orange was observed. The reaction mixture was filtered, concentrated, and washed with pentane (3×4 mL), and **3** was isolated as an orange powder (218 mg, 76% yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 73.29 (d, $^4J_{\text{PP}} = 4$ Hz), 19.88 (d, $^4J_{\text{PP}} = 4$ Hz); ^1H NMR (400 MHz, CD_2Cl_2) δ 8.06 (dd, $^3J_{\text{PH}} = 12.6$, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.82–7.68 (m, 2H), 7.59 (dd, $^2J_{\text{HH}} = 16.1$, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 7.56–7.46 (m, 2H), 7.40 (td, $^3J_{\text{HH}} = 7.4$, $^4J_{\text{HH}} = 1.3$ Hz, 1H), 7.35–7.27 (m, 2H), 7.27–7.09 (m, 6H), 7.09–7.01 (m, 1H), 6.93 (ddd, $^2J_{\text{PH}} = 10.8$, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 1.4$ Hz, 1H), 6.75 (td, $^3J_{\text{HH}} = 7.2$, $^4J_{\text{HH}} = 3.9$ Hz, 1H), 6.69–6.57 (m, 1H), 1.37 (d, $^4J_{\text{PH}} = 1.9$ Hz, 15H), 1.13 (d, $^4J_{\text{PH}} = 2.0$ Hz, 15H); $^1\text{H}\{^{31}\text{P}\}$ NMR (400 MHz, CD_2Cl_2) δ 8.06 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.77–7.73 (m, 2H), 7.59 (dd, $^2J_{\text{HH}} = 14.9$, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 7.53–7.48 (m, 2H), 7.43–7.37 (m, 2H), 7.31 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H), 7.25–7.11 (m, 7H), 7.05 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 6.93 (dd, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 1.4$ Hz, 1H), 6.74 (td, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 1.0$ Hz, 1H), 6.62 (td, $^3J_{\text{HH}} = 7.5$, $^4J_{\text{HH}} = 1.6$ Hz, 1H), 1.38 (s, 15H), 1.13 (s, 15H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2) δ 153.23 (dd, $J_{\text{PC}} = 14.2$, $J_{\text{PC}} = 13.6$ Hz), 144.82 (d, $J_{\text{PC}} = 85.4$ Hz), 140.95 (dd, $J_{\text{PC}} = 11.5$, $J_{\text{PC}} = 2.5$ Hz), 139.56 (d, $J_{\text{PC}} = 65.0$ Hz), 137.81 (dd, $J_{\text{PC}} = 65.3$, $J_{\text{PC}} = 2.2$ Hz), 133.68 (d, $J_{\text{PC}} = 10.5$ Hz), 133.52 (d, $J_{\text{PC}} = 14.2$ Hz), 132.39 (d, $J_{\text{PC}} = 10.3$ Hz), 132.25 (d, $J_{\text{PC}} = 11.0$ Hz), 131.29 (d, $J_{\text{PC}} = 11.7$ Hz), 130.61 (d, $J_{\text{PC}} = 2.5$ Hz), 128.76 (d, $J_{\text{PC}} = 2.6$ Hz), 128.69 (d, $J_{\text{PC}} = 2.8$ Hz), 128.35–127.68 (m), 127.23 (d, $J_{\text{PC}} = 10.6$ Hz), 127.22 (d, $J_{\text{PC}} = 10.7$ Hz), 126.16 (d, $J_{\text{PC}} = 11.6$ Hz), 120.67 (d, $J_{\text{PC}} = 14.5$ Hz), 93.67 (d, $^3J_{\text{PC}} = 3.2$ Hz), 91.34 (d, $^3J_{\text{PC}} = 2.7$ Hz), 8.60 (s), 8.44 (s). HR MS (FD^+): m/z calcd for $\text{C}_{44}\text{H}_{49}\text{ClIr}_2\text{N}_2\text{O}_2\text{P}_2\text{S}$ $[\text{M}]^+$ 1150.19136, observed 1150.20248. Anal. Calcd for $\text{C}_{44}\text{H}_{49}\text{ClIr}_2\text{N}_2\text{O}_2\text{P}_2\text{S}$: C, 45.88; H, 4.29; N, 2.43. Found: C, 45.67; H, 4.39, N, 2.39.

Synthesis of 4. Complex **3** (23 mg, 0.02 mmol) was dissolved in 1 mL of CH_2Cl_2 , and 1 equiv of HCl (20 μL of 1 M solution in diethyl ether) was added. The reaction mixture turned from orange to yellow and was stirred for 1 h, concentrated, and washed with 1 mL of pentane ($3 \times$). Complex **4** was obtained quantitatively as a yellow solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 80.43 (s), 35.15 (s); ^1H NMR (300 MHz, CD_2Cl_2) δ 9.26 (br s, 1H), 7.91 (dd, $^3J_{\text{PH}} = 13.3$, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.70 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H), 7.59–7.46 (m, 3H), 7.45–7.28 (m, 10H), 7.10–6.87 (m, 4H), 1.40 (d, $^4J_{\text{PH}} = 2.1$ Hz, 15H), 1.16 (d, $^4J_{\text{PH}} = 2.3$ Hz, 15H); $^1\text{H}\{^{31}\text{P}\}$ NMR (400 MHz, CD_2Cl_2) δ 9.26 (s, 1H), 7.91 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.70 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H), 7.59–7.46 (m, 3H), 7.45–7.28 (m, 10H), 7.10–6.87 (m, 4H), 1.40 (s, 15H), 1.16 (s, 15H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2) δ 149.71 (t, $J_{\text{PC}} = 12.0$ Hz), 141.40 (d, $J_{\text{PC}} = 11.7$ Hz), 134.90 (d, $J_{\text{PC}} = 63.9$ Hz), 133.33 (d, $J_{\text{PC}} = 61.65$ Hz), 133.01 (d, $J_{\text{PC}} = 11.4$ Hz), 132.68 (d, $J_{\text{PC}} = 2.5$ Hz), 132.33 (d, $J_{\text{PC}} = 12.2$ Hz), 132.13 (d, $J_{\text{PC}} = 11.7$ Hz), 131.75 (d, $J_{\text{PC}} = 12.0$ Hz), 131.55 (d, $J_{\text{PC}} = 2.8$ Hz), 131.46 (d, $J_{\text{PC}} = 2.6$ Hz), 130.32 (s), 129.23 (d, $J_{\text{PC}} = 11.4$ Hz), 128.91 (br. s), 128.51 (d, $J_{\text{PC}} =$

11.5 Hz), 127.93 (d, $J_{\text{PC}} = 12.1$ Hz), 127.22 (d, $J_{\text{PC}} = 64.7$ Hz), 123.25 (d, $J_{\text{PC}} = 15.0$ Hz), 97.07 (d, $^3J_{\text{PC}} = 3.2$ Hz), 93.71 (d, $^3J_{\text{PC}} = 2.7$ Hz), 8.98 (s), 8.90 (d, $^4J_{\text{PC}} = 0.7$ Hz). HR MS (FD^+): m/z calcd for $\text{C}_{44}\text{H}_{50}\text{ClIr}_2\text{N}_2\text{O}_2\text{P}_2\text{S}_1 [\text{M-Cl}]^+$ 1152.2093452, observed 1152.41311.

Synthesis of 5. Complex **3** (23 mg, 0.02 mmol) was dissolved in 0.2 mL of CD_2Cl_2 and 0.4 mL of $\text{THF-}d_8$ in a J-Young NMR tube. The NMR tube was rigorously purged and pressurized with 5 bar of H_2 and heated to 50 $^\circ\text{C}$ for 20 h. The bright-yellow reaction mixture turned slightly darker, and the quantitative formation of **5** was observed by NMR spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CD}_2\text{Cl}_2/\text{THF-}d_8$, 1:2) δ 67.74 (s), 28.58 (s); ^{31}P NMR (162 MHz, $\text{CD}_2\text{Cl}_2/\text{THF-}d_8$, 1:2) δ 67.74 (d, $^2J_{\text{PH}} = 32.3$ Hz), 28.57 (s); ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{THF-}d_8$, 1:2) δ 7.96 (dd, $^3J_{\text{HH}} = 8.8$, $^3J_{\text{PH}} = 8.8$ Hz, 1H), 7.74 (d, $^4J_{\text{PH}} = 2.0$ Hz, 1H), 7.72–7.65 (m, 2H), 7.34–7.28 (m, 4H), 7.27–7.16 (m, 6H), 7.11–7.03 (m, 2H), 6.99 (td, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 2.6$ Hz, 2H), 6.86 (dt, $^3J_{\text{HH}} = 7.7$, $^4J_{\text{HH}} = 3.5$ Hz, 1H), 6.61 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 1.39 (d, $^4J_{\text{PH}} = 1.4$ Hz, 15H), 1.03 (d, $^4J_{\text{PH}} = 2.3$ Hz, 15H), –15.48 (d, $^4J_{\text{PH}} = 35.1$ Hz, 1H); $^1\text{H}\{^{31}\text{P}\}$ NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{THF-}d_8$, 1:2) δ 7.96 (d, $^3J_{\text{HH}} = 8.8$ Hz, 1H), 7.74 (s, 1H), 7.72–7.65 (m, 2H), 7.34–7.28 (m, 4H), 7.27–7.16 (m, 6H), 7.11–7.03 (m, 2H), 6.99 (td, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 2.6$ Hz, 2H), 6.86 (t, $^3J_{\text{HH}} = 7.7$, 1H), 6.61 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 1.39 (s, 15H), 1.03 (s, 15H) –15.48 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $\text{CD}_2\text{Cl}_2/\text{THF-}d_8$, 1:2) δ 147.33 (s), 140.90 (s), 134.37 (d, $J_{\text{PC}} = 12.7$ Hz), 134.20 (d, $J_{\text{PC}} = 12.3$ Hz), 133.52 (d, $J_{\text{PC}} = 72.1$ Hz), 132.33 (d, $J_{\text{PC}} = 56.0$ Hz), 131.32 (d, $J_{\text{PC}} = 2.2$ Hz), 131.24 (d, $J_{\text{PC}} = 2.3$ Hz), 128.68 (s), 126.82 (s), 96.31 (d, $^3J_{\text{PC}} = 2.6$ Hz), 94.27 (d, $^3J_{\text{PC}} = 3.6$ Hz), 35.87 (s), 33.99 (s), 22.88 (s), 13.99 (s), 9.00 (s). HR MS (ESI^+): m/z calcd For $\text{C}_{44}\text{H}_{50}\text{ClIr}_2\text{N}_2\text{O}_2\text{P}_2\text{S}_1 [\text{M-H}]^+$ 1153.2004, observed 1153.2080. In the absence of a H_2 atmosphere, compound **5** decomposed rapidly in contact with air, preventing accurate bulk purity analysis and isolation in pure form.

Computational Details. Geometry optimizations were carried out with the Turbomole program package, coupled to the PQS Baker optimizer via the BOpt package, at the spin unrestricted ri-DFT level using the BP86 functional, the resolution-of-identity (ri) method, and the def2-TZVP basis set for the geometry optimizations.¹³

X-ray Crystal Structure Determination. X-ray intensities were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) (**3**) or on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator ($\lambda = 0.71073$ Å) and a CMOS Photon 50 detector at a temperature of 150(2) K (**1**). Intensity data were integrated with the Eval15 software or the Bruker APEX2 software.^{14a} Absorption correction and scaling was performed with SADABS.^{14b} The structures were solved with the programs SHELXT^{14c} (complex **3**) or SHELXTL (**1**).^{14a} Least-squares refinement was performed with SHELXL-2013^{14c} against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Metal bound hydrogen atom H11 in complex **4** was refined freely with an isotropic displacement parameter, all other hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.^{14d} Crystallographic data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ligand 1. $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2\text{P}_2\text{S}$, FW = 464.43, colorless block, $0.24 \times 0.24 \times 0.10$ mm³, orthorhombic, *Pbcn* (No. 60), $a = 26.023(3)$, $b = 9.7154(9)$, $c = 9.0650(9)$ Å, $V = 2291.8(4)$ Å³, $Z = 4$, $D_x = 1.346$ g/cm³, $\mu = 0.305$ mm^{−1}; 21954 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.59$ Å^{−1}; 2026 reflections were unique ($R_{\text{int}} = 0.024$), of which 1669 were observed [$I > 2\sigma(I)$]; 191 parameters were refined with 200 restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0425/0.0858. $R1/wR2$ [all reffs]: 0.0567/0.0918. $S = 1.178$. Residual electron density between −0.30 and 0.24 e/Å³. CCDC: 1045424.

Complex 3. $\text{C}_{44}\text{H}_{49}\text{ClIr}_2\text{N}_2\text{O}_2\text{P}_2\text{S}$ + disordered solvent, FW = 1151.70[*], orange block, $0.27 \times 0.21 \times 0.16$ mm³, orthorhombic, $P2_12_12_1$ (No. 19), $a = 14.517(2)$, $b = 16.851(3)$, $c = 19.123(3)$ Å, $V = 4678.0(13)$ Å³, $Z = 4$, $D_x = 1.635$ g/cm³[*], $\mu = 5.89$ mm^{−1}[*]; 50481 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65$ Å^{−1} at a temperature of 150(2) K. Intensities were integrated using the

SAINT software.^{14c} Absorption correction and scaling based on multiple measured reflections was performed with SADABS^{14f} (0.49–0.75 correction range); 10736 reflections were unique ($R_{\text{int}} = 0.023$), of which 10429 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using the program SHELXT.^{14g}

The crystal structure of **3** contains voids (806 Å³/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was taken into account by back-Fourier transformation with the SQUEEZE routine^{14h} in PLATON,¹⁴ⁱ resulting in 148 electrons/unit cell. Refinement in space group $P2_12_12_1$ was done as an inversion twin, resulting in a twin fraction (Flack parameter^{14j}) of 0.496(6). The SHELXL-2013 software^{14c} was used for the least-squares refinement against F^2 of all reflections. The Cp* ligand at Ir₂ and the noncoordinated phenyl at P₂₁ were refined with a disorder model. The carbon atoms of the disordered Cp* were refined with isotropic displacement parameters. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model; 537 parameters were refined with 405 restraints concerning the disordered groups (displacement parameters, residue flatness, distances, and angles). $R1/wR2$ [$I > 2\sigma(I)$]: 0.0189/0.0418. $R1/wR2$ [all reffs]: 0.0200/0.0421. $S = 1.134$. Residual electron density between –0.79 and 0.74 e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.¹⁴ⁱ CCDC: 1047332. The [*] indicates that derived values do not contain the contribution of the disordered solvent molecules.

■ ASSOCIATED CONTENT

■ Supporting Information

NMR spectra and DFT optimized structure of **4'**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00249.

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■ Notes

The authors declare no competing financial interest.

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