

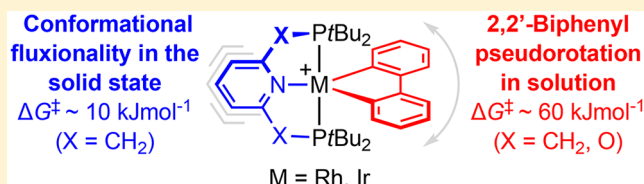
Synthesis and Structural Dynamics of Five-Coordinate Rh(III) and Ir(III) PNP and PONOP Pincer Complexes

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S Supporting Information

ABSTRACT: The synthesis and characterization of a homologous series of five-coordinate rhodium(III) and iridium(III) complexes of PNP (2,6-(*t*Bu₂PCH₂)₂C₅H₃N) and PONOP (2,6-(*t*Bu₂PO)₂C₅H₃N) pincer ligands are described: [M(PNP)(biph)][BAR^F₄] (M = Rh, **1a**; Ir, **1b**; biph = 2,2'-biphenyl; Ar^F = 3,5-(CF₃)₂C₆H₃) and [M-(PONOP)(biph)][BAR^F₄] (M = Rh, **2a**; Ir, **2b**). These complexes are structurally dynamic in solution, exhibiting pseudorotation of the biph ligand on the ¹H NMR time scale (ΔG^\ddagger ca. 60 kJ mol⁻¹) and, in the case of the flexible PNP complexes, undergoing interconversion between helical and puckered pincer ligand conformations (ΔG^\ddagger ca. 10 kJ mol⁻¹). Remarkably, the latter is sufficiently facile that it persists in the solid state, leading to temperature-dependent disorder in the associated X-ray crystal structures. Reaction of **1** and **2** with CO occurs for the iridium congeners **1b** and **2b**, leading to the formation of sterically congested carbonyl derivatives.



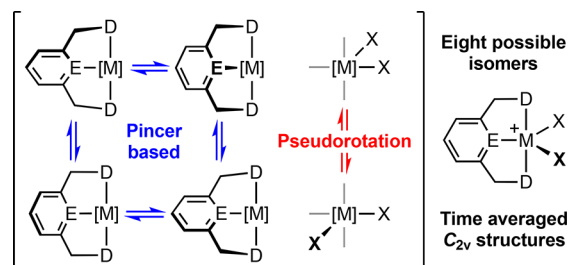
INTRODUCTION

Pincers are a prominent ligand class in organometallic chemistry and catalysis, conferring thermal stability while permitting a wide range of metal-based reactivity.¹ As prospective intermediates in stoichiometric and catalytic reactions, the structure and reactivity of five-coordinate rhodium(III) and iridium(III) derivatives are of fundamental mechanistic interest, although the inherent high reactivity of these species can preclude isolation.^{2,3} Coupled with these difficulties, the capacity of coordinatively unsaturated pincer complexes for rapid structural dynamics can encumber accurate structural elucidation in solution and, correspondingly, mechanistic interpretation of any ensuing onward reactivity. In general terms, the associated dynamics can be deconvoluted into (a) pincer ligand-centered processes and (b) pseudorotation of the reactive ligands about the metal (Scheme 1). In the context of the former, atropisomerism of

the characteristically C₂ twisted geometries of methylene-bridged DED ligands is particularly noteworthy and has been studied in detail for late transition metal complexes of NHC-based CEC ligands.^{4,5} Catalytically important iridium(III) dihydride complexes of phosphine-based pincer ligands are prominent fluxional group 9 examples, exhibiting time-averaged C_{2v} symmetry in solution, both for flexible PEP (i.e., (a) + (b) dynamics) and rigid POEOP (i.e., (b) dynamics) pincer ligands.^{6,7}

As a platform to systematically study the dynamic properties of low-coordinate group 9 pincer complexes, we herein report on the synthesis, characterization, and reactivity of a new homologous series of five-coordinate rhodium(III) and iridium(III) 2,2'-biphenyl (biph) complexes of flexible PNP (2,6-(*t*Bu₂PCH₂)₂C₅H₃N) and rigid PONOP (2,6-(*t*Bu₂PO)₂C₅H₃N) pincer ligands: [M(PNP)(biph)][BAR^F₄] (M = Rh, **1a**; Ir, **1b**; Ar^F = 3,5-(CF₃)₂C₆H₃) and [M(PONOP)(biph)][BAR^F₄] (M = Rh, **2a**; Ir, **2b**; Chart 1). As part of ongoing work in our laboratories exploring the organometallic chemistry of NHC-based pincers,⁸ we have recently prepared CNC analogues A and B.⁹ In these complexes, biph pseudorotation is inhibited by the macrocyclic CNC pincer ligand, but slow atropisomerism on the ¹H NMR (600 MHz) time scale was established using experiments that detect magnetization transfer. As further precedent, five-coordinate iridium(III) 2,2'-biphenyl complexes of neutral PCP complexes (C, D) have previously been reported by Krogh-Jespersen, Goldman, and co-workers.^{10,11}

Scheme 1. Structural Dynamics of Five-Coordinate DED Pincer Complexes in Solution^a

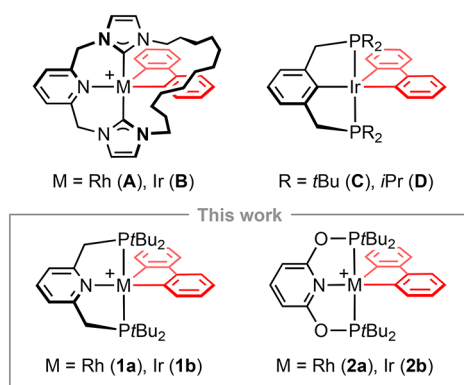


^aM = Rh, Ir; E = N, C⁻; X = high trans influence, reactive anionic ligand.

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Chart 1. Rhodium and Iridium Pincer Complexes of 2,2'-Biphenyl^a

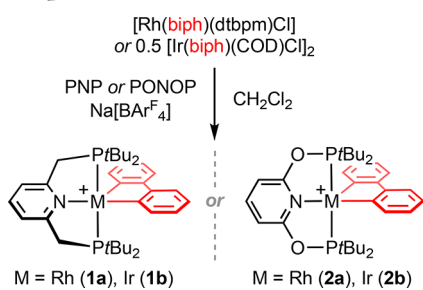


^a[BAR^F₄]⁻ counter anions omitted for clarity.

RESULTS AND DISCUSSION

Exploiting precursors first described by Jones and Crabtree¹² and procedures developed in our laboratories,^{9,13} synthesis of the target PNP and PONOP derivatives **1** and **2** was achieved through reactions of [Rh(biph)(dtbpm)Cl] (dtbpm = bis(*tert*-butylphosphino)methane) or [Ir(biph)(COD)Cl]₂ (COD = 1,5-cyclooctadiene) with the desired pincer ligand in CH₂Cl₂ solution in the presence of Na[BAR^F₄] as a halide abstracting agent (Scheme 2).¹⁴ The resulting five-coordinate complexes were all isolated as microcrystalline materials of high purity in good to excellent yield (79–87%) and extensively characterized in solution and the solid state (vide infra). Employment of this procedure notably avoids the need for late-stage C–C bond activation of biphenylene or double C–H bond activation of biphenyl associated with the formation of **C** and **D**^{10,11} and moreover benefits from the use of common and more widely applicable Rh(III)(biph) and Ir(III)(biph) precursors.

Scheme 2. Synthesis of Rh(III) and Ir(III) PNP and PONOP Complexes **1** and **2**^a



^a[BAR^F₄]⁻ counter anions omitted for clarity.

Single crystalline samples of **1** and **2** suitable for inter-rogation by X-ray diffraction were obtained in all cases, with the homologous metal pairs **1a,b** and **2a,b** being isomorphous. The structures of **1b** and **2b** (determined at 150 K) are shown in Figure 1, with key metrics for the complete set provided in Table 1. The solid-state structures are notable for pseudosquare pyramidal metal geometries about the metal, with near-ideal N20–M–C15 but distinctly obtuse P2–M1–P3 angles (**1**, ca. 164°; **2**, ca. 160°). In each case, one of the *tert*-butyl substituents is canted toward the vacant coordination site and

characterized by M1...H–C29 contacts of 3.001(3)–3.072(3) Å and reduced M1–P2–C28 angles of 104.11(9)–107.05(10)°. These features mark out the formation of weak agostic interactions,¹⁵ decreasing in the order **1b** > **1a** > **2b** > **2a**, although contrasting those observed for **A** and **B** (M...H–C contacts of 2.978(5)–3.000(3) Å), meaningful 3c–2e bonding was not substantiated by ATR IR spectroscopy. Consistent with these experimental observations, natural bond orbital (NBO) analysis of optimized geometries of **1** and **2** indicates the associated NBO perturbation energies are considerably less than those in **A** and **B** and of very low absolute magnitude ($\sum \Delta E^2/kJ \text{ mol}^{-1}$: **1a**, 26.8; **1b**, 42.3; **2a**, 11.0; **2b**, 22.0; cf. **A**, 79.3; **B**, 107.9; see the Supporting Information).^{9,16} On the basis of these data, the yawing of the phosphine donors is therefore best reconciled by steric buttressing between the biph ligand and the proximal *tert*-butyl substituents rather than a consequence of agostic bonding with the metal. Coordination of biph is associated with a disparity between the M1–C4 and M1–C15 bond lengths (ca. 3 pm) expected for the presence of an open coordination site trans to the former.

Close inspection of the solid-state structures of **1** determined at 150 K revealed the presence of minor disordered components that could be satisfactorily modeled as conformational isomers, where the pincer is coordinated in a puckered C_s symmetric manner (conferring overall C_s symmetry; **1-C_s**) instead of the helical C₂ symmetry found for the major component (conferring overall C₁ symmetry; **1-C₁**). Binding of this nature is not uncommon for platinum group metal PNP pincer complexes (22% frequency, CSD v5.40), with a number of prominent rhodium and iridium examples.^{2,17} Recognizing that this disorder could be the manifestation of structural dynamics in the solid state,¹⁸ additional crystallographic data were collected across a wide temperature range (75–250 K), for both the rhodium and iridium congeners, and subsequently refined using a disorder model involving both helical and puckered pincer binding modes (Figure 2). From these data, it can be concluded that dynamic equilibration between these two pincer ligand conformations does indeed occur in the solid state: with the former conformation enthalpically favored and exclusively observed at 75 K (within the error of the experiment) but entropically disfavored over the latter, which commands a significant fraction of the model at 250 K (**1a**, 29%; **1b**, 33%).

A van't Hoff analysis of the equilibrium temperature dependence enabled the associated thermodynamic parameters to be extracted: **1a**, $\Delta H = +2.0 \pm 0.1 \text{ kJ mol}^{-1}$, $\Delta S = +0.4 \pm 0.9 \text{ J K}^{-1} \text{ mol}^{-1}$ ($\Delta G_{298\text{K}} = +1.9 \pm 0.4 \text{ kJ mol}^{-1}$); **1b**, $\Delta H = +2.0 \pm 0.1 \text{ kJ mol}^{-1}$, $\Delta S = +1.7 \pm 0.9 \text{ J K}^{-1} \text{ mol}^{-1}$ ($\Delta G_{298\text{K}} = +1.5 \pm 0.4 \text{ kJ mol}^{-1}$). No statistically significant differences can be inferred for the congeners, but the trend is for the isomerization to be less endergonic for **1b**. This suggestion is supported by a DFT-based computational analysis at the ω B97X-D3 level of theory,¹⁹ although the calculations are unable to reproduce the relative energetics of the isomers in silico: **1a**, $\Delta G_{298\text{K}} = -0.7 \text{ kJ mol}^{-1}$; **1b**, $\Delta G_{298\text{K}} = -2.1 \text{ kJ mol}^{-1}$. More importantly, the calculations affirm a very small energy difference between the alternative ligand conformations with low associated activation barriers (**1a**, $\Delta G^\ddagger = 8.4 \text{ kJ mol}^{-1}$; **1b**, $\Delta G^\ddagger = 9.8 \text{ kJ mol}^{-1}$), congruous with fluxionality in the solid state. Combined, the experimental and computational data suggest that C₂ and C_s symmetric binding of PNP ligands is nearly isoenergetic and rapid interconversion between these

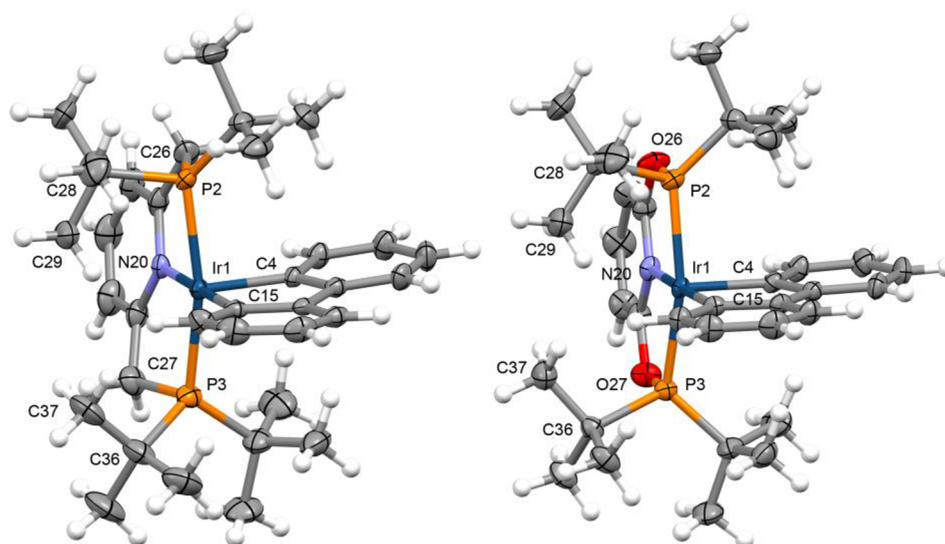


Figure 1. Solid-state structures of **1b** (left) and **2b** (right) determined at 150 K. Thermal ellipsoids drawn at 50% probability; minor disordered component in **1b**, solvent in **2b**, and anions omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2** Determined at 150 K

metric	PNP ^a		PONOP	
	M = Rh (1a)	M = Ir (1b)	M = Rh (2a)	M = Ir (2b)
M1–P2	2.3047(6)	2.3076(6)	2.3201(6)	2.3099(7)
M1–P3	2.3797(6)	2.3612(7)	2.3384(6)	2.3326(6)
M1–N20	2.130(2)	2.123(2)	2.096(2)	2.096(2)
M1–C4	1.988(2)	2.001(2)	1.996(2)	2.013(2)
M1–C15	2.023(2)	2.040(2)	2.021(2)	2.044(2)
M1–C29	3.025(3)	3.001(3)	3.072(3)	3.031(3)
P2–M1–P3	164.49(2)	163.74(2)	160.59(2)	159.75(2)
N20–M1–C15	178.40(8)	178.85(9)	177.97(9)	177.47(9)
M1–P2–C28	104.27(8)	104.11(9)	107.05(10)	106.58(10)

^aMetrics associated with major disordered component (1-C₁) only.

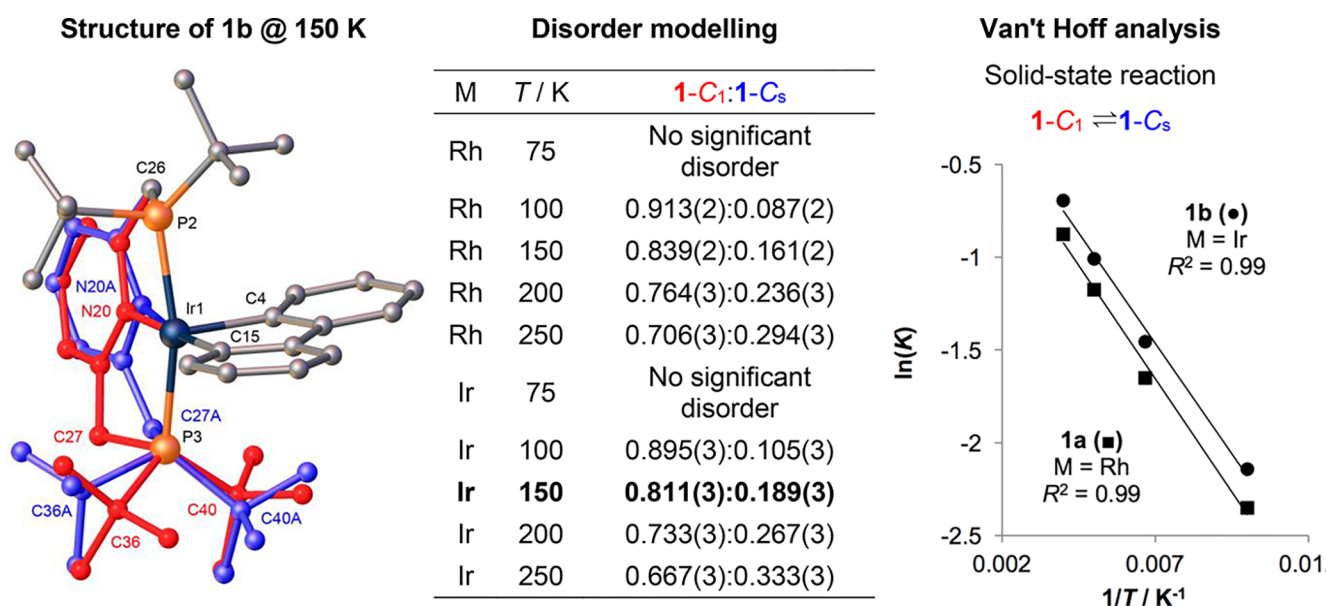


Figure 2. Solid-state dynamics of **1** interrogated by X-ray crystallography.

modes is implicit, to the extent that these processes can even occur in the confined environment of a crystal lattice at cryogenic temperatures!

The solution-phase structure and dynamics of **1** and **2** were investigated in CD_2Cl_2 solution using multinuclear and variable-temperature NMR spectroscopy (500 MHz, 185–308 K). All complexes are markedly fluxional, with the dynamics notably manifested in ^1H NMR spectra measured at 298 K by line broadening of the biph, CH_2 (PNP), and *t*Bu signals, with varying degrees of coalescence from overall C_s to C_{2v} symmetry that we attribute to pseudorotation of the biph ligand on the NMR time scale. In the case of **1a**, the fast exchange regime was reached upon heating to 308 K, resulting in a fully C_{2v} symmetric ^1H NMR spectrum, whereas cooling to 250 K resulted in a sharp C_s symmetric ^1H NMR spectrum (Figure 3). Although full signal coalescence could not be

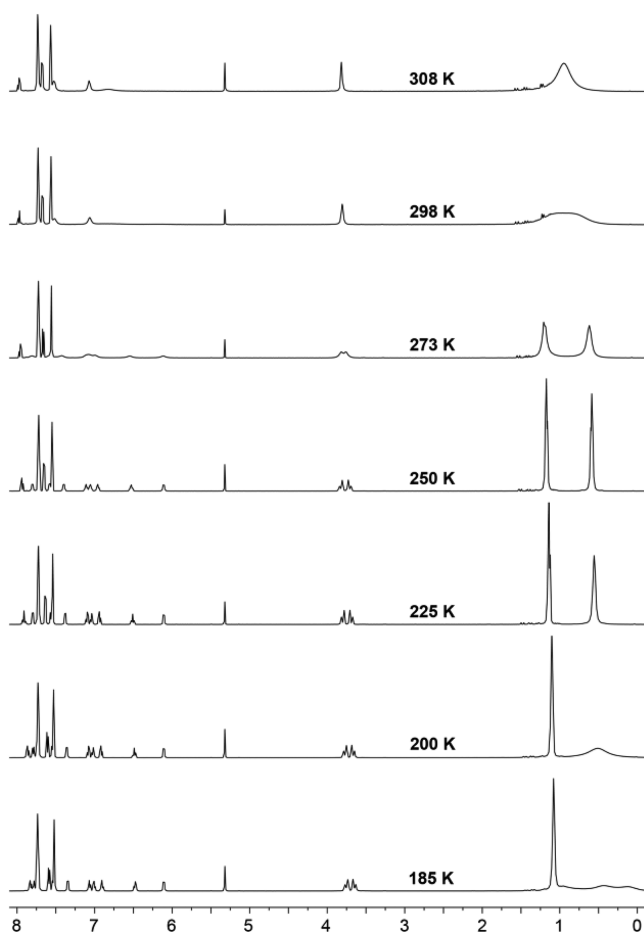


Figure 3. Variable-temperature ^1H NMR spectra of **1a** (CD_2Cl_2 , 500 MHz).

achieved within the physical limits of the solvent for **1b** or **2**, simulation of the associated variable-temperature ^1H NMR spectra using gNMR enabled the activation parameters associated with the pseudorotation to be determined for all four complexes (Table 2).²⁰ These data substantiate more facile pseudorotation in **1a** compared to the other pincer complexes, which are notable for very similar activation barriers, ΔG^\ddagger ca. 60 kJ mol^{-1} .

The measured activation barriers for the pseudorotation are well reproduced computationally at the $\omega\text{B97X-D3}$ level of theory (Table 2). For both pincer ligands, this rotation was

Table 2. Activation Barriers for the Pseudorotation Observed in **1** and **2** and Computational Models

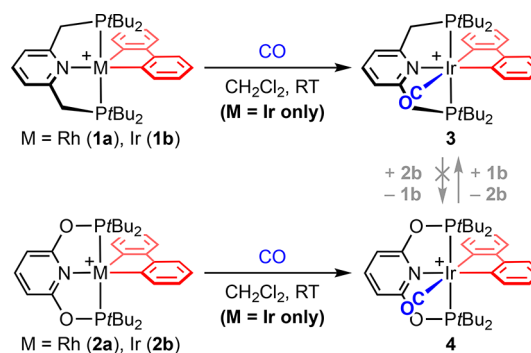
ΔG^\ddagger (kJ mol^{-1})	1a	1b	2a	2b
experiment	56 ± 1	62 ± 1	58 ± 4	60 ± 4
full model	53.7	59.8	59.6	58.6
truncated model	21.2	21.7	20.4	18.2

found to proceed via distinctly C_2 symmetric trigonal bipyramidal transition states and relatively flat potential energy surfaces (absolute vibrational modes all $<40 \text{ cm}^{-1}$). Adoption of the associated twisted pincer ligand geometries is necessary to minimize steric buttressing between *tert*-butyl substituents and the biph ligand, but these interactions are still significantly destabilizing. Supporting this assertion, the corresponding barriers for computational models featuring methyl instead of *tert*-butyl substituents are significantly lower (Table 2). Moreover, from the reported ^1H NMR data at ambient temperature (400 MHz), the barrier associated with pseudorotation in **D** (C_{2v}) is considerably less than for less sterically congested **C** (C_s).¹¹

Overall, C_s symmetry is retained in the ^1H NMR spectra of **1** and **2** in CD_2Cl_2 on cooling to 185 K and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these complexes exhibit single sharp resonances across the full temperature range studied—**1a**, δ 44.2; **1b**, δ 27.0; **2a**, δ 179.8; **2b**, δ 157.7 (298 K)—with those of the rhodium congeners notable for coupling to ^{103}Rh (**1a**, $^1J_{\text{RhP}} = 110 \text{ Hz}$; **2a**, $^1J_{\text{RhP}} = 114 \text{ Hz}$). In the context of the pincer ligand conformations adopted in **1**, these data do not enable us to definitely discriminate between time-averaged or static C_s symmetric pincer binding, although on the basis of the dynamics observed in the solid state, the former is inferred. Cooling to low temperature does, however, impart the presence of restricted rotation in one of the two sets of *tert*-butyl groups (**1a**, $\Delta G^\ddagger = 37 \pm 3 \text{ kJ mol}^{-1}$; **1b**, $\Delta G^\ddagger = 38 \pm 4 \text{ kJ mol}^{-1}$). This hindered rotation could potentially be the manifestation of agostic bonding; however, none of the three decoalesced signals are shifted to appreciably low frequency and we correspondingly assign these *tert*-butyl groups to those proximal to the biph moiety. This assertion is supported by the observation of similar behavior in the carbonyl derivative **4** (vide infra).

The reactions of **1** and **2** with CO (1 atm) were studied in CD_2Cl_2 . Although sluggish, addition of CO occurs to the iridium pincers at ambient temperature, conferring carbonyl derivatives **3** ($t = 6 \text{ h}$) and **4** ($t = 2 \text{ days}$) in quantitative

Scheme 3. Reactions of **1** and **2** with CO^a



^a[BAR^{F}_4][−] counter anions omitted for clarity.

spectroscopic yield (**3**, $\delta_{31\text{P}}$ 24.7; **4**, $\delta_{31\text{P}}$ 147.3; Scheme 3). Both were subsequently isolated and fully characterized. No reactions resulted in the case of the lighter congeners, and this observation is borne out in the computationally derived thermodynamics, which indicates that the associated rhodium carbonyl derivatives are not formed with sufficiently exothermic enthalpies (cf. periodic trends apparent from Table 3) to offset the considerably unfavorable entropic

Table 3. Carbonyl Stretching Frequencies of PNP and PONOP Complexes (CH₂Cl₂)

complex	$\nu(\text{CO})$ (cm ⁻¹)
[Rh(PNP)(CO)][BAR ^F ₄]	1990
[Rh(PONOP)(CO)][BAR ^F ₄]	2016
[Ir(PNP)(CO)][BAR ^F ₄]	1977
[Ir(PONOP)(CO)][BAR ^F ₄]	2003
3	2028
4	2033

penalties associated with reactions of this type (calculated ΔS ca. -179 J mol⁻¹ K⁻¹; $-298 \times \Delta S$ ca. $+53$ kJ mol⁻¹). Calculated $\Delta G_{298\text{K}}$ values increase in the order **1b** (-28.8 kJ mol⁻¹) < **2b** (-10.6 kJ mol⁻¹) < **1a** ($+26.1$ kJ mol⁻¹) < **2a** ($+47.5$ kJ mol⁻¹), with the relative energetics of the iridium complexes confirmed by crossover experiments involving heating mixtures of **3/2b** (no reaction observed after 55 days at 50 °C) and **4/1b** (affords **3/2b** in 99% conversion after 55 days at 50 °C).

The solid-state structure of **4** is notable for a significantly contorted metal coordination geometry compared to **3**, as gauged by significant deviation of the N20–Ir1–C15 angle from linearity ($163.83(9)^\circ$ cf. $173.9(2)^\circ$) and acute N20–Ir1–C4 angle ($83.69(9)^\circ$ cf. $94.2(2)^\circ$; Figure 4). This marked deviation from ideal geometry presumably results from steric congestion around the carbonyl ligand enforced by the rigid nature of the pincer backbone, and this suggestion is supported in solution by restricted rotation of the *tert*-butyl substituents

proximal to the biph ligand on the ¹H NMR time scale (CD₂Cl₂, 500 MHz; $\Delta G^\ddagger = 41 \pm 3$ kJ mol⁻¹; assignment confirmed by a NOESY experiment). The carbonyl stretching band measured for **4** (2033 cm⁻¹) is slightly elevated in comparison to that of **3** (2028 cm⁻¹), but the variance is considerably less than that for the corresponding Ir(I) carbonyl pincers measured under the same conditions (Table 3). Combined, these data highlight the pivotal role of steric buttressing in the differences in thermodynamics and kinetics of carbonyl addition to PNP-ligated **1b** compared to PONOP-ligated **2b**.

In the context of dynamics of the PNP pincer ligand, line broadening of the resonances associated with the phosphine donor groups that signals the onset of decoalescence from overall C_s to C₁ symmetry (i.e., helical pincer binding) is apparent for **3** on cooling to low temperature (298 to 185 K) by ¹H and ³¹P NMR spectroscopy in CD₂Cl₂ solution (500 MHz). This behavior indicates considerably less favorable pincer ligand dynamics in coordinatively saturated **3** in comparison to its unsaturated parent complex **1b**. Consistent with this suggestion, the X-ray derived structure of **3** is notable for well-ordered helical coordination of the PNP ligand (within the error of the experiment) at 150 K (cf. **1b**, vide supra).

CONCLUSIONS

Exploiting facile substitution reactions of [Rh(biph)(dtbpm)-Cl] and [Ir(biph)(COD)Cl]₂, the expedient and high-yielding synthesis of a homologous series of five-coordinate rhodium(III) and iridium(III) complexes of PNP (2,6-(*t*Bu₂PCH₂)₂C₅H₃N) and PONOP (2,6-(*t*Bu₂PO)₂C₅H₃N) pincer ligands has been described: [M(PNP)(biph)][BAR^F₄] (M = Rh, **1a**; Ir, **1b**) and [M(PONOP)(biph)][BAR^F₄] (M = Rh, **2a**; Ir, **2b**). These complexes display interesting structural dynamics in solution involving pseudorotation of the biph ligand on the ¹H NMR time scale (ΔG^\ddagger ca. 60 kJ mol⁻¹) and, in the case of the flexible PNP complexes, interconversion between helical and puckered pincer ligand conformations

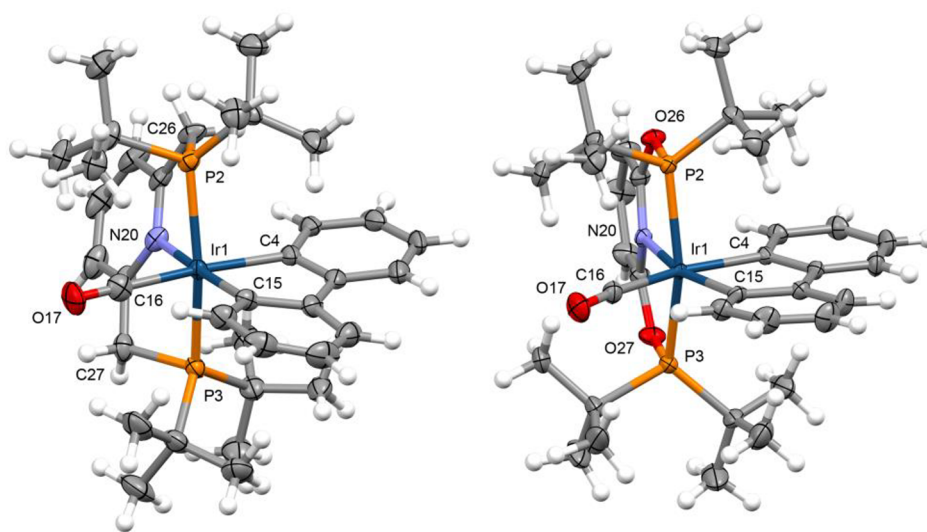


Figure 4. Solid-state structures of **3** (left) and **4** (right) determined at 150 K. Thermal ellipsoids drawn at 50% probability; anions omitted. Selected bond lengths (Å) and angles (deg): **3**, Ir1–P2, 2.3812(12); Ir1–P3, 2.4144(12); Ir1–C4, 2.110(4); Ir1–C15, 2.066(4); Ir1–C16, 1.927(5); Ir1–N20, 2.143(3); P2–Ir1–P3, 161.20(4); C4–Ir1–C16, 171.8(2); N20–Ir1–C15, 173.9(2); **4**, Ir1–P2, 2.3644(6); Ir1–P3, 2.3828(6); Ir1–C4, 2.113(2); Ir1–C15, 2.085(2); Ir1–C16, 1.920(3); Ir1–N20, 2.128(2); P2–Ir1–P3, 157.82(2); C4–Ir1–C16, 166.78(10); N20–Ir1–C15, 163.83(9).

(ΔG^\ddagger ca. 10 kJ mol⁻¹). Interrogation in silico suggests the former process involves overall C₂ symmetric transition states, with twisted PNP and PONOP pincer ligand binding geometries, that are significantly destabilized by steric buttressing between the *tert*-butyl phosphine substituents and the biph ligand. Remarkably, the latter process is sufficiently facile that it persists in the solid state, leading to temperature-dependent disorder in the associated X-ray crystal structures. Reaction of **1** and **2** with CO occurs for the iridium congeners **1b** and **2b**, leading to the formation of sterically congested carbonyl derivatives.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed under an atmosphere of argon using Schlenk and glovebox techniques unless otherwise stated. Glassware was oven-dried at 150 °C overnight and flame-dried under a vacuum prior to use. Molecular sieves were activated by heating at 300 °C in vacuo overnight. CD₂Cl₂ was freeze–pump–thaw degassed and dried over 3 Å molecular sieves. Other anhydrous solvents were purchased from Acros Organics or Sigma-Aldrich, freeze–pump–thaw degassed, and stored over 3 Å molecular sieves. PNP,²¹ PONOP,²² Na[BAR^F₄],^{14c} [Rh(biph)-(dtbpm)Cl]₂^{12a} and [Ir(biph)(COD)Cl]₂,^{12b} and [M(pincer)(CO)]-[BAR^F₄]^{17a,23} were synthesized according to published procedures, or minor variations thereof. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on Bruker Maxis Plus (HR) or Agilent 6130B single Quad (LR) instruments. Infrared spectra were recorded on a PerkinElmer Spectrum 100 using a KBr transmission cell in CH₂Cl₂. Microanalyses were performed at the London Metropolitan University by Stephen Boyer.

Preparation of [Rh(PNP)(biph)][BAR^F₄] (1a). A suspension of PNP (87.9 mg, 222 μmol), [Rh(biph)(dtbpm)Cl] (132 mg, 222 μmol), and Na[BAR^F₄] (197 mg, 222 μmol) in CH₂Cl₂ (2 mL) was stirred at ambient temperature for 16 h, filtered, and the filtrate reduced to dryness in vacuo. The resulting orange solid was washed with pentane and dried to give a microcrystalline orange solid. Yield: 293 mg (87%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution at ambient temperature.

¹H NMR (500 MHz, CD₂Cl₂): δ 7.97 (t, ³J_{HH} = 7.8, 1H, py), 7.71–7.75 (m, 8H, Ar^F), 7.67 (d, ³J_{HH} = 7.8, 2H, py), 7.56 (br, 4H, Ar^F), 7.52 (br, 2H, biph), 7.06 (br, 2H, biph), 5.8–7.3 (vbr m, 4H, biph), 3.81 (br, 4H, CH₂), 1.07 (vbr, fwhm = 180 Hz, 18H, *t*Bu), 0.81 (vbr, fwhm = 180 Hz, 18H, *t*Bu).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂, selected data only): δ 162.4 (vt, J_{PC} = 3, py), 140.9 (s, py), 123.4 (vt, J_{PC} = 4, py), 36.3 (vt, J_{PC} = 8, CH₂).

³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 44.2 (d, ¹J_{RhP} = 111).

HR ESI-MS (positive ion, 4 kV): 650.2543, [M]⁺ (calcd 650.2546) *m/z*.

Anal. Calcd for C₆₇H₆₃BF₂₄NP₂Rh (1513.87 g mol⁻¹): C, 53.16; H, 4.19; N, 0.93; Found: C, 53.05; H, 4.17; N, 0.90.

Preparation of [Ir(PNP)(biph)][BAR^F₄] (1b). A suspension of PNP (81.1 mg, 205 μmol), [Ir(biph)(COD)Cl]₂ (100 mg, 103 μmol), and Na[BAR^F₄] (182 mg, 205 μmol) in CH₂Cl₂ (2 mL) was stirred at ambient temperature for 16 h, filtered, and the filtrate reduced to dryness in vacuo. The resulting red solid was washed with pentane and dried to give a microcrystalline red solid. Yield: 141 mg (86%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution at ambient temperature.

¹H NMR (500 MHz, CD₂Cl₂): δ 8.02 (t, ³J_{HH} = 7.9, 1H, py), 7.75 (d, ³J_{HH} = 7.9, 2H, py), 7.71–7.80 (m, 9H, Ar^F + biph), 7.61 (br, 1H, biph), 7.56 (br, 4H, Ar^F), 7.34 (br, 1H, biph), 7.07 (br, 2H, 2 × biph), 6.88 (br, 1H, biph), 6.37 (br, 1H, biph), 5.80 (br, 1H, biph),

3.80 (vt, J_{PH} = 4.1, 4H, CH₂), 1.19 (br, 18H, *t*Bu), 0.64 (br, 18H, *t*Bu).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂, selected data only): δ 164.2 (vt, J_{PC} = 3, py), 140.3 (s, py), 123.1 (vt, J_{PC} = 4, py), 37.3 (vt, J_{PC} = 11, CH₂), 30.6 (br, *t*Bu{CH₃}), 28.6 (br, *t*Bu{CH₃}).

³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 27.0.

HR ESI-MS (positive ion, 4 kV): 740.3110, [M]⁺ (calcd 740.3122) *m/z*.

Anal. Calcd for C₆₇H₆₃BF₂₄IrNP₂ (1603.18 g mol⁻¹): C, 50.20; H, 3.96; N, 0.87; Found: C, 50.28; H, 3.88; N, 0.85.

Preparation of [Rh(PONOP)(biph)][BAR^F₄] (2a). A suspension of PONOP (30.0 mg, 75.1 μmol), [Rh(biph)(dtbpm)Cl] (44.6 mg, 75.0 μmol), and Na[BAR^F₄] (66.6 mg, 75.2 μmol) in CH₂Cl₂ (2 mL) was stirred at ambient temperature for 16 h, filtered, and the filtrate reduced to dryness in vacuo. The resulting orange solid was washed with pentane and dried to give a microcrystalline orange solid. Yield: 96.8 mg (85%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution at ambient temperature.

¹H NMR (500 MHz, CD₂Cl₂): δ 8.14 (t, ³J_{HH} = 8.2, 1H, py), 7.70–7.77 (m, 9H Ar^F + biph), 7.59 (br, 2H, biph), 7.56 (br, 4H, Ar^F), 7.20 (d, ³J_{HH} = 8.2, 2H, py), 7.11 (br, 3H, 3 × biph), 6.54 (vbr, fwhm = 120 Hz, 1H, biph), 5.83 (vbr, fwhm = 95 Hz, 1H, biph), 1.29 (vbr, fwhm = 125 Hz, 18H, *t*Bu), 0.79 (vbr, fwhm = 125 Hz, 18H, *t*Bu).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂, selected data only): δ 162.3 (vt, J_{PC} = 1, py), 147.2 (s, py), 106.1 (vt, J_{PC} = 2, py).

³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 179.8 (d, ¹J_{RhP} = 114).

HR ESI-MS (positive ion, 4 kV): 654.2128, [M]⁺ (calcd 654.2132) *m/z*.

Anal. Calcd for C₆₅H₅₉BF₂₄NO₂P₂Rh (1517.82 g mol⁻¹): C, 51.44; H, 3.92; N, 0.92; Found: C, 51.23; H, 3.62; N, 0.90.

Preparation of [Ir(PONOP)(biph)][BAR^F₄] (2b). A suspension of PONOP (30.0 mg, 75.1 μmol), [Ir(biph)(COD)Cl]₂ (36.7 mg, 37.6 μmol), and Na[BAR^F₄] (66.6 mg, 75.2 μmol) in CH₂Cl₂ (2 mL) was stirred at ambient temperature for 16 h, filtered, and the filtrate reduced to dryness in vacuo. The resulting red solid was washed with pentane and dried to give a microcrystalline red solid. Yield: 48.1 mg (79%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution at ambient temperature.

¹H NMR (500 MHz, CD₂Cl₂): δ 8.14 (t, ³J_{HH} = 8.2, 1H, py), 7.70–7.76 (m, 8H, Ar^F), 7.65 (br, 2H, 2 × biph), 7.56 (br, 4H, Ar^F), 7.42 (br, 1H, biph), 7.28 (d, ³J_{HH} = 8.2, 2H, py), 7.10 (br, 2H, 2 × biph), 6.97 (br, 1H, biph), 6.33 (br, 1H, biph), 5.55 (br, 1H, biph), 1.28 (br, 18H, *t*Bu), 0.76 (br, 18H, *t*Bu).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂, selected data only): δ 162.9 (br, py), 146.5 (s, py), 105.6 (vt, J_{PC} = 2, py), 28.8 (br, *t*Bu{CH₃}), 27.6 (br, *t*Bu{CH₃}).

³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 157.7.

HR ESI-MS (positive ion, 4 kV): 744.2705, [M]⁺ (calcd 744.2707) *m/z*.

Anal. Calcd for C₆₅H₅₉BF₂₄IrNO₂P₂ (1607.13 g mol⁻¹): C, 48.58; H, 3.70; N, 0.87; Found: C, 48.36; H, 3.48; N, 0.88.

NMR Scale Reactions of 1 and 2 with CO. A 20 mM solution of **1/2** in CD₂Cl₂ (0.5 mL) prepared in a J. Young's valve NMR tube was freeze–pump–thaw degassed, placed under an atmosphere of carbon monoxide (1 atm), gently shaken at ambient temperature, and monitored periodically using ¹H and ³¹P NMR spectroscopy. Quantitative conversion of **1b** to **3** (*t* = 6 h) and **2b** to **4** (*t* = 2 days) resulted. No reaction was observed in the case of **1a** and **2a** after 24 h (even after heating at 50 °C for an additional 24 h).

Preparation of [Ir(PNP)(biph)(CO)][BAR^F₄] (3). A solution of **1b** (16.0 mg, 9.98 μmol) in CD₂Cl₂ (0.5 mL) was placed under an atmosphere of carbon monoxide (1 atm) and gently shaken for 6 h at ambient temperature (as above). The solvent was removed in vacuo to afford a white solid. Yield: 16.0 mg (99%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH₂Cl₂ solution at ambient temperature.

Table 4. Variable-Temperature ^1H NMR Data

complex	exchange	rate of exchange (s^{-1})						
		308 K	298 K	273 K	250 K	225 K	200 K	185 K
1a	biph	2310	661	90	11			
1a	<i>t</i> Bu					4728	1008	266
1b	biph	224	101	10	1			
1b	<i>t</i> Bu					2554	297	205
2a	biph	759	342	38	16			
2b	biph	259	179	24	5			
4	<i>t</i> Bu					1094	44	16

^1H NMR (500 MHz, CD_2Cl_2): δ 8.00 (t, $^3J_{\text{HH}} = 7.9$, 1H, py), 7.96 (d, $^3J_{\text{HH}} = 8.2$, 1H, biph), 7.70–7.75 (m, 8H, Ar^F), 7.68 (d, $^3J_{\text{HH}} = 7.9$, 2H, py), 7.62 (d, $^3J_{\text{HH}} = 7.6$, 1H, biph), 7.58 (d, $^3J_{\text{HH}} = 7.9$, 1H, biph), 7.56 (br, 4H, Ar^F), 7.12 (t, $^3J_{\text{HH}} = 7.8$, 1H, biph), 7.10 (t, $^3J_{\text{HH}} = 7.9$, 1H, biph), 7.00 (t, $^3J_{\text{HH}} = 7.4$, 1H, biph), 6.91 (t, $^3J_{\text{HH}} = 7.4$, 1H, biph), 6.81 (d, $^3J_{\text{HH}} = 7.5$, 1H, biph), 4.30 (dvt, $^2J_{\text{HH}} = 17.0$, $J_{\text{PH}} = 4.1$, 2H, CH_2), 3.72 (dvt, $^2J_{\text{HH}} = 17.0$, $J_{\text{PH}} = 3.5$, 2H, CH_2), 1.27 (vt, $J_{\text{PH}} = 7.2$, 18H, *t*Bu), 0.62 (vt, $J_{\text{PH}} = 7.4$, 18H, *t*Bu).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 180.3 (t, $^2J_{\text{PC}} = 7$, CO), 163.0 (br, py), 162.3 (q, $^1J_{\text{CB}} = 50$, Ar^F), 159.5 (s, biph), 153.4 (s, biph), 141.8 (t, $^2J_{\text{PC}} = 10$, biph), 141.7 (s, py), 139.1 (s, biph), 137.5 (s, biph), 135.4 (br, Ar^F), 131.3 (t, $^2J_{\text{PC}} = 6$, biph), 129.4 (qq, $^1J_{\text{FC}} = 32$, $^1J_{\text{CB}} = 3$, Ar^F), 128.2 (s, biph), 126.7 (s, biph), 126.2 (s, biph), 125.2 (q, $^1J_{\text{FC}} = 272$, CF_3), 124.7 (s, biph), 123.5 (vt, $J_{\text{PC}} = 4$, py), 122.5 (s, biph), 122.1 (s, biph), 118.0 (sept, $^3J_{\text{FC}} = 4$, Ar^F), 40.8 (vt, $J_{\text{PC}} = 10$, *t*Bu{C}), 40.1 (vt, $J_{\text{PC}} = 9$, *t*Bu{C}), 40.0 (vt, $J_{\text{PC}} = 11$, CH_2), 30.8 (br, *t*Bu{CH₃}), 30.2 (br, *t*Bu{CH₃}).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 24.7.

HR ESI-MS (positive ion, 4 kV): 768.3064, $[\text{M}]^+$ (calcd 768.3072) *m/z*.

Anal. Calcd for $\text{C}_{66}\text{H}_{63}\text{BF}_{24}\text{IrNOP}_2$ (1631.19 g mol⁻¹): C, 50.07; H, 3.89; N, 0.86; Found: C, 50.14; H, 3.74; N, 0.80.

Preparation of $[\text{Ir}(\text{PONOP})(\text{biph})(\text{CO})][\text{BAR}_4]$ (4). A solution of **2b** (16.1 mg, 10.0 μmol) in CD_2Cl_2 (0.5 mL) was placed under an atmosphere of carbon monoxide (1 atm) and gently shaken for 2 days at ambient temperature (as above). The solvent was removed in vacuo to afford a white solid. Yield: 16.0 mg (98%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at ambient temperature.

^1H NMR (500 MHz, CD_2Cl_2): δ 8.13 (t, $^3J_{\text{HH}} = 8.2$, 1H, py), 7.97 (d, $^3J_{\text{HH}} = 7.7$, 1H, biph), 7.67–7.78 (m, 9H, Ar^F + biph), 7.56 (br, 4H, Ar^F), 7.20 (d, $^3J_{\text{HH}} = 8.2$, 2H, py), 7.18 (d, $^3J_{\text{HH}} = 7.2$, 1H, biph), 7.12 (t, $^3J_{\text{HH}} = 7.5$, 1H, biph), 7.05 (t, $^3J_{\text{HH}} = 7.6$, 1H, biph), 6.75 (t, $^3J_{\text{HH}} = 7.5$, 1H, biph), 5.19 (d, $^3J_{\text{HH}} = 7.8$, 1H, biph), 1.54 (vt, $J_{\text{PH}} = 7.7$, 18H, *t*Bu), 0.69 (vt, $J_{\text{PH}} = 8.5$, 18H, *t*Bu).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 180.9 (t, $^2J_{\text{PC}} = 9$, CO), 162.3 (br, py), 162.3 (q, $^1J_{\text{CB}} = 50$, Ar^F), 156.5 (s, biph), 152.9 (s, biph), 147.5 (s, py), 143.2 (weak, biph), 135.4 (br, Ar^F + biph), 134.5 (s, biph), 129.7 (observed, biph), 129.4 (qq, $^1J_{\text{FC}} = 32$, $^1J_{\text{CB}} = 3$, Ar^F), 128.7 (s, biph), 128.0 (s, biph), 127.3 (s, biph), 125.8 (s, biph), 125.2 (q, $^1J_{\text{FC}} = 272$, CF_3), 123.8 (s, biph), 123.4 (s, biph), 118.0 (sept, $^3J_{\text{FC}} = 4$, Ar^F), 106.0 (vt, $J_{\text{PC}} = 2$, py), 46.4 (vt, $J_{\text{PC}} = 9$, *t*Bu{C}), 45.7 (vt, $J_{\text{PC}} = 9$, *t*Bu{C}), 29.4 (br, *t*Bu{CH₃}), 28.8 (vt, $J_{\text{PC}} = 2$, *t*Bu{CH₃}).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 147.3.

HR ESI-MS (positive ion, 4 kV): 772.2659, $[\text{M}]^+$ (calcd 772.2657) *m/z*.

Anal. Calcd for $\text{C}_{66}\text{H}_{59}\text{BF}_{24}\text{IrNO}_3\text{P}_2$ (1635.14 g mol⁻¹): C, 48.48; H, 3.64; N, 0.86; Found: C, 48.42; H, 3.60; N, 0.89.

Crossover Experiments. A solution of **1b** (16.0 mg, 9.98 μmol) and **4** (16.4 mg, 10.0 μmol) in CD_2Cl_2 (0.5 mL) prepared in a J. Young's valve NMR tube was heated at 50 °C and periodically monitored by ^1H and ^{31}P NMR spectroscopy. Slow conversion to **2b** and **3** was observed, with a 99:1 mixture of **2b**,**3**:**1b**,**4** obtained after 55 days.

A solution of **2b** (16.1 mg, 10.0 μmol) and **3** (16.3 mg, 10.0 μmol) in CD_2Cl_2 (0.5 mL) prepared in a J. Young's valve NMR tube was

heated at 50 °C and periodically monitored by ^1H and ^{31}P NMR spectroscopy. No reaction was apparent after 55 days.

Variable-Temperature NMR Experiments. Analysis was performed using 20 mM solutions of the pincer complexes in CD_2Cl_2 (0.5 mL) prepared in J. Young's valve NMR tubes. Samples were equilibrated at the required temperature for a period of 10 min before spectra were acquired (^1H , 500 MHz; ^{31}P , 202 MHz). Exchange processes observed by ^1H NMR spectroscopy were simulated using gNMR,²⁰ with reference line widths and values of J_{PH} fixed following analysis of low temperature data (Table 4, Supporting Information). Activation parameters were determined using the equation $\Delta G^\ddagger = RT[23.760 + \ln(T/k_{\text{exchange}})]$; reported values and errors are based on a statistical analysis of at least three different temperature points.

Crystallography. Data were collected on a Rigaku Oxford Diffraction SuperNova AtlasS2 CCD diffractometer using graphite monochromated Mo K α or Cu K α radiation and an Oxford Cryosystems N-Helix cryostat. Data were collected and reduced using CrysAlisPro.²⁴ The structures were solved using SHELXT and refined using SHELXL, through the Olex2 interface.^{25,26} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using the riding model.

Variable-temperature data for **1a** and **1b** were collected for unique crystals at 75, 100, 150, 200, and 250 K but in a nonsequential order. Samples were conditioned for at least 30 min, with longer times for the lowest temperature measurements (1 h 45 min at 75 K). No significant disorder was apparent from the refined data collected at 75 K, with no Fourier peaks around the pincer methylene bridges >0.7 e \AA^{-3} . Disorder of the pincer ligand at the other temperatures, evident from inspection of the thermal parameters and presence of Fourier peaks around the pincer methylene bridges ≥ 1.0 e \AA^{-3} , was systematically treated by modeling part of the ligand over two sites and restraining its geometry (Figure 2). Rigid body constraints were applied for the pyridine moiety. In this way, the R_1 indices were significantly lowered (Supporting Information, Table S1) and sensible thermal parameters obtained in all cases.

Full details for all structures reported are documented in the CIF, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1901989–1902010.

Computational. Starting from geometries of the cations observed in the solid state, optimizations were carried out using Grimme's dispersion corrected $\omega\text{B97X-D3}$ functional¹⁹ as implemented in ORCA 4.0.1.2, with the def2-TZVPP basis set, and associated def2-ECP on Rh/Ir, and the def2-TZVP(-f) basis set on all other atoms.²⁷ Minima and saddle points were verified by analytical vibrational mode analysis at the same level of theory, which also provided thermochemical corrections. A scalar relativistic all-electron single point energy calculation was subsequently carried out using the $\omega\text{B97X-D3}$ functional within the ZORA approximation and using the corresponding basis sets (Rh, old-ZORA-TZVPP; Ir, SARC-ZORA-TZVPP; all other atoms, ZORA-def2-TZVP(-f)).²⁸ NBO analyses were carried out using NBO 6.0.¹⁶

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00957.

NMR, IR, and ESI-MS spectra of new compounds, NMR spectra of selected reactions, selected crystallographic parameters for **1a** and **1b** (Table S1), calculated thermodynamic values, and NBO analysis of **1** and **2** (PDF)

Optimized geometries (XYZ)

Primary NMR data (ZIP)

Accession Codes

CCDC 1901989–1902010 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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