Rhodium(III) and Iridium(III) Complexes of a NHC-Based Macrocycle: Persistent Weak Agostic Interactions and Reactions with Dihydrogen

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ABSTRACT: The synthesis and characterization of five-coordinate rhodium(III) and iridium(III) 2,2′-biphenyl complexes [M(CNC-12)(biph)][BArF₄] (M = Rh (1a), Ir (1b)), featuring the macrocyclic lutidine- and NHC-based pincer ligand CNC-12 are reported. In the solid state these complexes are notable for the adoption of weak ε-agostic interactions that are characterized by M···H−C contacts of ca. 3.0 Å by X-ray crystallography and ν(CH) bands of reduced wavenumber by ATR IR spectroscopy. Remarkably, these interactions persist on dissolution and were observed at room temperature using NMR spectroscopy (CD₂Cl₂) and solution-phase IR spectroscopy (CCl₄). The associated metrics point toward a stronger M···H−C interaction in the iridium congener, and this conclusion is borne out on interrogation of 1 in silico using DFT-based NBO and QTAIM analyses. Reaction of 1 with dihydrogen resulted in hydrogenolysis of the biaryl and formation of fluxional hydride complexes, whose ground state formulations as [Rh(CNC-12)H₂][BArF₄] (2a″) and [Ir(CNC-12)H₂(H₂)][BArF₄] (2b‴) are proposed on the basis of inversion recovery and variable-temperature NMR experiments, alongside a computational analysis. Reactions of 1 and 2 with carbon monoxide help support their respective structural properties.

INTRODUCTION

Conferring high thermal stability and supporting a wide range of metal-based reactivity, mer-tridentate “pincer” ligands have become ubiquitous in contemporary organometallic chemistry and homogeneous catalysis. Examples featuring terminal phosphine donors are prototypical, but driven by favorable bonding and steric characteristics, N-heterocyclic carbene (NHC) congeners are attracting growing interest. In addition to their successful use as ancillary ligands in a wide variety of transition-metal-catalyzed reactions, their coordination has also been shown to confer useful photophysical and electrochemical properties. Curiously and despite the enduring prominence of these metals in homogeneous catalysis, the organometallic chemistry of rhodium and iridium complexes of NHC-based pincer ligands is significantly underdeveloped. Indeed, current knowledge is largely confined to oxidative addition reactions of alkyl halides and other strong oxidants with CNC pincer complexes (Figure 1). Underlying this paucity, the potential of modern synthetic protocols for accessing NHC adducts of suitably reactive rhodium- and iridium-containing fragments is only now starting to be realized. For instance, building upon a comparative study of the efficacy of coinage metal transfer agents, we have recently reported the synthesis of labile rhodium(I) ethylene complexes C and D through transmetalation reactions of the respective copper(I) derivatives with [Rh(C₂H₄)₂Cl]₂. These complexes act as latent sources of reactive three-coordinate Rh(I) fragments and promote selective terminal alkyne coupling reactions, following initial and facile C(sp)−H bond activation.

In the context of advancing the organometallic chemistry of group 9 NHC-based pincers, and informed by preceding work in our laboratories, in this report we describe the straightforward synthesis, isolation, and characterization of low-coordinate rhodium(III) and iridium(III) 2,2′-biphenyl complexes [M(CNC-12)(biph)][BArF₄] (M = Rh (1a), Ir (1b)).
stabilized by adoption of agostic interactions 12 and serve as precursors for catalytically relevant hydride derivatives 2 through hydrogenolysis of the biaryl. The structure and reactivity of these metal hydrides are contrasted with the aid of DFT calculations.

RESULTS AND DISCUSSION

Exploiting the aforementioned copper(I)-based transmetalation methodology, reactions between [Rh(biph)](dtbpm)Cl 13 (dtbpm = bis(di-tert-butylphosphino)methane) or [Ir(biph)- (COD)Cl] 2 (COD = 1,5-cyclooctadiene) 14 and [Cu(CNC-12)][BARF 4] 7 were employed for the preparation of 1 (Scheme 1). These reactions resulted in quantitative transfer of the pincer to the platinum-group metal; however, in the case of the rhodium(III) derivative, formation of a copper(I) diphosphine byproduct necessitated addition of excess Na[BARF 4] to ensure complete removal of the halogen ion. The formally independent cations are provided in Table 1. Including the use of single-crystal X-ray crystallography.

Single crystals of 1 were obtained by recrystallization from CH 2 Cl 2/hexane at room temperature, although with different morphologies (1a, P1 with Z′ = 1; 1b, P 2 1/c with Z′ = 2; Figure 2 and Table 1). Despite these lattice differences, both feature a common molecular structure for all the corresponding cations that is characterized by C 2 symmetry, a square-based-pyramidal geometry about the metal, and a skewed dodecamethylene chain that is distorted in such a manner as to enable formation of an ε-agostic interaction (M···H–C ca. 3.0 Å). Coordination of 2,2′-biphenyl is associated with a considerable disparity between the trans C···H···M–C(biph) and N–M–C(biph) bond lengths (ca. 2 pm). Combined, these metrics point to weak M···H–C interactions 9,12 however, the contorted nature of the macrocycle suggests that they nevertheless play an important stabilizing role. Comparison between the structurally related rhodium and iridium cations indicates there is a trend toward shorter M···H–C contacts in the heavier congeners, but the difference is not statistically significant within the data set collected. The adoption of meaningful agostic interactions in the solid-state is supported by ATR IR spectroscopy (Figures S7 and S20), 15 with broad υ(CH) bands of reduced wavenumber observed for 1a (2682 cm −1 ) and, supporting the trend for stronger agostic interactions in the third-row congener noted by X-ray crystallography, to a greater extent 1b (2571 cm −1 ). These bands are not observed in the corresponding carbonyl derivatives (3; vide infra).

In order to further interrogate the nature of the M···H–C interactions observed in the solid state for 1, we turned to DFT-based computational methods. Cations of 1 were optimized at the ωB97X-D3 level of theory and analyzed using the natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) approaches (Table 2). 16–18 In both cases, the presence of stabilizing agostic interactions in 1 is corroborated through identification of significant NBO perturbation energies associated with σ CH → ML σ* and ML → σ σ* σ* CH bonding, with the former contributions particularly pronounced in comparison to the latter, and associated

![Figure 2. Solid-state structures of 1a (left) and 1b (right, only one unique cation shown). Thermal ellipsoids are drawn at 50% probability; solvent molecules, anions, minor disordered components, and most hydrogen atoms are omitted for clarity. Key metrics for all crystallographically independent cations are provided in Table 1.](image-url)
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Table 2. Calculated Geometric, NBO, and QTAIM Properties of 1

|                | 1a (M = Rh) | 1b (M = Ir) |
|----------------|-------------|-------------|
| M⋯H⋯C/A       | 2.22        | 2.17        |
| M⋯H⋯C/d       | 3.10        | 3.04        |
| \(\Delta M\)  | 133.7       | 132.1       |
| \(\Delta E(\sigma_{CH}\rightarrow M^*)/kcal mol^{-1}\) | 11.83 | 18.68 |
| \(\Delta E(M^*\rightarrow \sigma_{CH})/kcal mol^{-1}\) | 7.15 | 7.13 |
| occ \(\sigma_{CH}\) NBO | 1.953 | 1.936 |
| occ \(\sigma^*_{CH}\) NBO | 0.023 | 0.027 |
| \(\rho(M\cdots-H\cdots-C)\) | 0.024 | 0.034 |
| \(\nu_{bf}(M\cdots-H\cdots-C)\) | +0.083 | +0.114 |
| \(K(M\cdots-H\cdots-C)\) | +0.002 | +0.001 |
| DI(M\cdots-H\cdots-C) | 0.114 | 0.130 |

Further evidence for the persistence of agostic interactions in solution was gathered using solution-phase IR spectroscopy: spectra of 1 recorded at room temperature in 

![Image](https://i.imgur.com/3965.png)

Further evidence for the persistence of agostic interactions in solution was gathered using solution-phase IR spectroscopy: spectra of 1 recorded at room temperature in CCl₄ show broad, reduced frequency \(\nu(CH)\) stretching bands (1a, 2694 cm\(^{-1}\); Figure 3; 1b, 2577 cm\(^{-1}\); Figure S21) that are not present in spectra of the respective carbonyl derivatives 3 (vide infra). Gratifyingly, these data are in good agreement with those collected in the solid state using ATR IR spectroscopy and strengthen the previous assertion regarding the relative strengths of the Ir⋯H⋯C and Rh⋯H⋯C interactions.

Supplementing the experimental and computational structural analyses, the electronic properties of 1 were probed by formation of the corresponding carbonyl adducts 3 (Scheme 2). These coordinate-saturated derivatives were straightforwardly prepared by reaction of 1 with carbon monoxide (1 atm), isolated in good yield, and fully characterized, including in the solid state using X-ray crystallography (3b (Z′ = 1) shown in Figure 4; 3a (Z′ = 2), CCDC 1862298). As a consequence of CO coordination, the solid-state structures of 3 show the expected displacement of the dodecamethylene chain away from the metal center and a significant increase in the opposing M⋯C(biph) bond lengths in comparison to 1 (3a, 2.068(3)/2.073(3) vs 1.992(3) Å; 3b, 2.106(2) vs 2.010(4)/2.018(4) Å), in line with trans-influence arguments. Stronger CO binding to iridium, in comparison to rhodium, is evident from the carbonyl stretching bands of 3 measured in CH₂Cl₂/CCl₄ solution, viz. 2050/2054 (3a) and 2018/2022 (3b) cm\(^{-1}\), and from a crossover experiment between 3a and 1b, where quantitative CO transfer from rhodium to iridium was observed by \(^1\)H NMR spectroscopy after heating in 1,2-

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Figure 4. Solid-state structure of 3b. Thermal ellipsoids are drawn at 50% probability; the anion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−C2, 2.106(2); Ir1−C13, 2.057(2); Ir1−C14, 1.916(2); Ir1−C28, 2.090(2); Ir1−C34, 2.097(2); C28−Ir1−C34, 174.25(6); Ir1−N20, 2.228(2). Equivalent metrics for 3a (Z′ = 2): Rh1−C2, 2.068(3); Rh1−C13, 2.054(3); Rh1−C14, 1.947(3); Rh1−C28, 2.100(3); Rh1−C34, 2.076(2); C28−Rh1−C34, 174.78(10); Rh1−N20, 2.230(2); Rh1−C102, 2.073(3); Rh1−C113, 2.041(3); Rh1−C114, 1.949(3); Rh1−C128, 2.099(3); Rh1−C134, 2.076(3); C128−Rh1−C134, 175.43(11); Rh1−N1120, 2.245(2).

difluorobenzene (DFB, Scheme 2).\(^{21,22}\) These data support the conclusion that stronger agostic interactions are formed in 1b in comparison to 1a. Moreover, complexes 3 also serve as useful references, helping confirm the spectroscopic features arising from the formation of agostic interactions, as noted above.

Hydrogenolysis of 2,2′-biphenyl proceeded quantitatively on reaction of 1 with dihydrogen (1 atm) at room temperature in CD₂Cl₂ (1a, 6 h; 1b, 24 h; Scheme 3). The structures and assignments of 2a as classical Rh(III) dihydride 2a\(^{″}\) (Scheme 3). Indeed, a structure of this formulation, stabilized by an ε-agostic interaction (ε-2a\(^{″}\)), is calculated to be the most thermodynamically preferred hydride derivative of 1a (B97X-D3 level of theory, Figure S5).\(^{24}\) The optimized structures of 2a\(^{″}\) and ε-2a\(^{″}\) exhibit square-based-pyramidal metal geometries, requiring the hydride ligands to be highly fluxional on the NMR time scale to reconcile the experimental findings.\(^{25,26}\) A plausible mechanism for such dynamics involves intermediate formation of C₃-symmetric Rh(1) dihydrogen complex 2a\(^{″}\), and the calculated barrier with respect to ε-2a\(^{″}\) is estimated to be only ΔG\(^{‡}\) = 3.8 kcal mol\(^{-1}\). Similar spectroscopic features were observed upon removal of hydrogen and placement under an atmosphere of argon, although the hydride resonance at δ −18.89 (T\(_{1}\) = 754 ± 23 ms) is notable for the exhibition of \(^{103}\)Rh coupling (J\(_{Rhh} = 40.6\) Hz) at 298 K. \(^{13}\)C NMR data for 2a were collected under argon, with the characteristics of the carbenic resonance at δ 182.8 (J\(_{Rhc} = 40\) Hz) notable for their similarity to those of five-coordinate Rh(III) 1a (ca. δ 175 (J\(_{Rhc} = 44\) Hz)), lending support to the assignment as 2a\(^{″}\).

As for the lighter congener, iridium hydride 2b is characterized by time-averaged C\(_{2v}\) symmetry under hydrogen at 298 K, with decoalescence of the CNC-12 \(^{1}\)H resonances on cooling to 200 K, indicative of fast atropisomerism of the pincer ligand. Differences, however, emerge on inspection of the hydride region of the \(^{1}\)H NMR spectra, where a significantly more downfield \(4\)H signal with considerably faster longitudinal relaxation is located at δ −9.46 (T\(_{1}\) = 94 ± 5 ms, fwhm = 230 Hz) at 298 K and δ −9.56 (T\(_{1}\) = 29 ± 3 ms, fwhm = 80 Hz) at 200 K. We correspondingly account for this behavior by assignment of 2b as the fluxional Ir(III) dihydride dihydrogen complex 2b\(^{″}\).\(^{26,27}\) This assignment is also borne out in silico, with a 2 step pathway via C\(_{2}\)-symmetric 2b\(^{‴}\) providing an upper bound for the associated barrier of fluxional exchange, ΔG\(^{‡}\) = 5.5 kcal mol\(^{-1}\). Interestingly, Ir(III) dihydride ε-2b\(^{″}\) (H\(_{2}\)) is predicted to be essentially isoenergetic with 2b\(^{″}\) (Figure S5),\(^{27}\) although the latter is presumably favored in the presence of excess dihydrogen. Indeed, consistent with the computed thermodynamics, removal of volatiles and redissolution under argon results in the emergence of a new C\(_{2v}\)-symmetric hydride complex at 298
K that exhibits a 2H resonance at δ = 24.53 with considerably slower longitudinal relaxation (T1 = 727 ± 16 ms), which we correspondingly assign to 2b″. This is the major species observed on attempted isolation of 2b from solution.

Reactions with carbon monoxide provided further insights into the structure and dynamics of 2, with 2a affording the known Rh(I) carbonyl complex B8 and 2b the novel Ir(III) dihydride carbonyl 4. The former reaction, trapping rhodium in the +1 oxidation state, provides a case for alternative ground-state assignment of 2a as Rh(I) dihydrogen complex 2a′ as opposed to Rh(II) dihydrogen 2a″. In the context of the preceding discussion, we reconcile this observation by dynamic equilibration between 2a″ and 2a″ in solution and faster/irreversible reaction of CO with the latter. The formation of 4, with diagnostic dihydride signals at δ = 7.33 (JHH = 2.9 Hz, T1 = 1120 ± 18 ms) and −17.69 (JHH = 2.9 Hz, T2 = 950 ± 9 ms) and a carbonyl stretching band at 2062 cm⁻¹, is more straightforwardly accounted for by direct reaction with 2b″ or substitution of 2b″, with both of these presumably in rapid dynamic equilibrium.

### CONCLUSIONS

Showing the effectiveness of copper-based transmetalation protocols, the straightforward preparation of mononuclear [Rh(CNC-12)(biph)(CO)]BF4 (M = Rh (3a), Ir (3b)) (B) and [Ir(CNC-12)2H2(CO)]BF4 (4), respectively.

### 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 vacuum prior to use. Molecular sieves were activated by heating at 300 °C in vacuo overnight. 1,2-Difluorobenzene was predried over Al2O3, distilled from calcium hydride, and dried twice over 3 Å molecular sieves. 22 CDCl3 was freeze–pump–thaw degassed and stored over 3 Å molecular sieves. Na[BArF4]28, [Rh(biph)(Cl)(dbt)][Cl]11, [Ir(biph)(Cl)(COD)]4 and [Cu(CNC-12)]2BF4 were synthesized according to published procedures. 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. NMR spectra in 1,2-difluorobenzene were recorded using an internal capillary of C6D6. 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 either a KBr transmission cell in CH2Cl2 or CCl4 or an ATR module fitted with a diamond/ZnSe crystal. Microanalyses were performed at the London Metropolitan University by Stephen Boyer.

**[Rh(CNC-12)(biph)][BF4]2 (1a).** A suspension of [Rh(biph)Cl(dbt)] (17.8 mg, 30.3 μmol), Na[BArF4] (13.9 mg, 56.5 μmol), and [Cu(CNC-12)]2BF4 (40.3 mg, 50.2 μmol) in CH2Cl2 (ca. 1 mL) was stirred until ambient temperature for 2 h, filtered, and the precipitate washed with CH2Cl2 (ca. 3 × 0.5 mL). Volatiles were removed in vacuo, and the product extracted into EtO (ca. 3 × 1 mL). (The ether-insoluble material appears to be a Cu(I) complex of dbt.) 31P[1H] NMR (162 MHz, CD2Cl2): δ 55.2 (s). The filtrate and washings were layered with hexane (ca. 20 mL) and stored at ambient temperature to afford the product as yellow blocks, which were isolated through decantation of the supernatant and dried in vacuo. Yield: 44.0 mg (95%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in CH2Cl2 at ambient temperature.

1H NMR (500 MHz, CD2Cl2): δ 8.01 (t, JHH = 7.7, H, py), 7.80 (d, JHH = 7.5, 1H, biph), 7.71–7.75 (m, 8H, ArH), 7.70 (d, JHH = 7.7, 1H, py), 7.58 (d, JHH = 7.7, 1H, py), 7.56 (br, ArH), 7.53 (d, JHH = 7.5, 1H, biph), 7.37 (d, JHH = 7.6, 1H, biph), 7.23 (br, 1H, NCH), 7.13 (t, JHH = 7.4, 1H, biph), 7.06 (t, JHH = 7.3, 1H, biph), 6.93 (t, JHH = 7.4, 1H, biph), 6.91 (br, 1H, NCH), 6.80 (br, 1H, NCH), 6.78 (br, 1H, NCH), 6.41 (t, JHH = 7.7, 1H, biph), 5.60 (dd, JHH = 7.8, 1H, biph), 5.49 (d, JHH = 15.6, 1H, pyCH3), 5.28 (d, JHH = 15.6, 1H, pyCH3), 5.25 (d, JHH = 15.6, 1H, CH3), 4.81–4.85 (dd, JHH = 13.9, 1H, H2CH, 11.2, 5.9, 1H, CH3), 4.80 (d, JHH = 15.6, 1H, CH3), 3.65 (dd, JHH = 13.6, 6.1, 1H, CH3), 2.98 (dd, JHH = 14.5, 10.7, 4.4, 1H, NCH), 2.58 (dd, JHH = 13.8, JHH = 4.2, 1H, NCH), 1.84–1.97 (m, 1H, CH3), 0.97–1.70 (m, 1H, CH3), 0.75–0.96 (m, 2H, 2H), 0.30–2.11 (m, 1H, CH3), 0.86 (m, 1H, CH3). 13C[1H] NMR (126 MHz, CD2Cl2): δ 176.0 (Jd/Hac = 44, NCN), 174.5 (d, Jd/Hac = 42, NCN), 163.8 (d, Jd/Hac = 38, biph), 162.3 (q, Jd/Hac = 50, ArH), 157.1 (s, py), 156.5 (s, py), 155.7 (d, Jd/Hac = 45, biph), 152.9 (d, Jd/Hac = 3, biph), 151.7 (d, Jd/Hac = 48, 141.2 (s, py), 138.5 (s, py), 135.4 (s, ArH), 132.8 (s, biph), 129.4 (q, Jd/Hac = 32, Jd/Hac = 3, ArH), 126.5 (s, py), 125.6 (d, Jd/Hac = 2, biph), 125.4 (d, Jd/Hac = 1, biph), 125.2 (q, Jd/Hac = 272, ArH), 125.1 (s, py), 124.1 (s, py), 124.0 (s, py), 112.5 (d, Jd/Hac = 3, biph), 121.4 (s, py), 121.2 (s, ArH), 122.2 (s, NCH), 121.6 (s, NCH), 122.1 (d, Jd/Hac = 2, biph), 118.0 (s, Jd/Hac = 4, Ar), 56.1 (s, pyCH2), 55.9 (s, pyCH2), 49.4 (s, NCH2), 47.8 (s, NCH2), 30.6 (s, CH3), 29.3 (s, CH2), 28.7 (s, CH2), 28.5 (s, CH2), 27.7 (CH3), 27.14 (s, CH3), 27.08 (s, CH3), 26.7 (s, CH3), 25.3 (s, CH3), 22.2 (s, CH2). IR (CH2Cl2): 3056, 2934, 2858, 2682 cm⁻¹. IR (CCl4): υ(CH) 3053, 2978, 2928, 2859, 2694 cm⁻¹. Anal. Calc. for C69H55BF24N5Rh: C, 51.28; H, 3.54; N, 4.24. Found: C, 51.17; H, 3.66; N, 4.15. HR ESI-MS (positive ion, 4 kV): 660.2566 (M+1, calc 660.2568) m/z.
diffraction were obtained by slow diffusion of hexane into a solution in CH2Cl2 at ambient temperature.

1H NMR (500 MHz, CD2Cl2): δ 8.04 (t, JHH = 7.7, 1H, py), 7.77–7.75 (m, 8H, Ar), 7.65 (vbr, fwhm = 50 Hz, 2H, py), 7.57 (br, 4H, Ar), 7.55 (d, JHH = 7.7, 1H, biph), 7.52 (d, JHH = 7.7, 1H, biph), 7.17 (t, JHH = 7.4, 1H, biph), 7.10 (t, JHH = 7.4, 1H, biph), 7.00 (observed vbr, 1H NCH), 6.98 (br, JHH = 7.4, 1H, biph), 6.84 (vbr, fwhm = 20 Hz, 2H, NCH), 6.51 (t, JHH = 7.4, 1H, biph), 5.76 (d, JHH = 7.6, 1H, biph), 5.37 (d, JHH = 148, 2H, pyCH2), 5.17 (vbr, fwhm = 120 Hz, 2H pyCH2+NCH), 4.80 (vbr, fwhm = 70 Hz, 1H, pyCH2), 2.88–3.44 (m, 4H, NCH), 1.81–1.70 (m, 4H, pyCH2). 13C{1H} NMR (126 MHz, CD2Cl2): 165.6 (br, NCN), 162.4 (q, 1C, biph), 153.8 (s, biph), 152.8 (s, biph), 150.3 (br, NCN), 147.6 (br, py), 147.3 (s, biph), 145.8 (s, biph), 144.3 (s, biph), 135.4 (s, ArF), 130.6 (s, biph), 129.4 (qq, 2C, ArF), 122.7 (s, ArF), 122.1 (s, NCH), 121.9 (s, NCH), 121.4 (s, biph), 121.0 (s, biph), 118.1 (sept, 3H, ArF), 115.6 (1H, pyCH2), 50.1 (br, NCH2), 48.6 (br, NCH2), 29.2 (s, CH2), 28.9 (br, CH2), 28.7 (br, CH2), 28.4 (br, CH2).

MS (positive ion, 4 kV): 660.2562 (∆m = 54.18; H, 3.57; N, 4.51. Found: C, 54.30; H, 3.76; N, 4.59. HR ESI-MS (positive ion, 4 kV): 778.3083 (M +), calc 778.3089 m/z).

**[Ir(CNC-12)(biph)(CO)][BArF4]** (1b). A suspension of [Ir(biph)(CO)](COD) (1.76 mg, 78.5 μmol) and Cu(CNC-12) [BArF4] (199.7 mg, 149.9 μmol) in CH2Cl2 (ca. 3 mL) was stirred at ambient temperature for 18 h and filtered and the precipitate washed with CH2Cl2 (3 × 1 mL). Volatiles were removed in vacuo, and the product recrystallized from EtOH/hexane (1/20, ca. 25 mL) to afford the product as a mixture of yellow needles and red blocks. Yield: 186.4 mg (77%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in CH2Cl2 at ambient temperature.

**[Ir(CNC-12)(biph)(CO)]** (1b) (160 mg, 9.92 μmol) and Ir(CNC-12)(biph)(CO) [BArF4] (1a) (1.67 mg, 9.92 μmol) in 1,2-C6H4F2 (ca. 0.5 mL) was heated at 90 °C for 18 h. Analysis by 1H NMR spectroscopy and LR ESI-MS indicated formation of a 1:1 mixture of [Rh(CNC-12)(biph)(CO)] [BArF4] (1a) and [Ir(CNC-12)(biph)(CO)] [BArF4] (1b), respectively.

**[Rh(CNC-12)(biph)(CO)] [BArF4]** (2a). A solution of [Rh(CNC-12)(biph)(CO)] [BArF4] (1a) (30.6 mg, 20.1 μmol) in CD3CN (ca. 0.5 mL) was freeze-pump–thaw degassed and used under an atmosphere of dihydrogen. The solution was mixed for 6 h at ambient temperature to afford the product quantitatively by NR spectroscopy.

**Crossover Experiment.** A solution of [Rh(CNC-12)(biph)(CO)] [BArF4] (1a) (15.4 mg, 9.92 μmol) and Ir(CNC-12)(biph)(CO) [BArF4] (1b) (160 mg, 9.92 μmol) in 1,2-C6H4F2 was degassed and placed under an atmosphere of CO to immediately afford a colorless solution. The volatiles were removed in vacuo, and the product recrystallized from CH2Cl2/hexane (1/15, ca. 15 mL) to afford the title compound as colorless blocks, which were isolated through decantation of the supernatant and dried in vacuo. Yield: 41.7 mg (85%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in CH2Cl2 at ambient temperature.

**[Ir(CNC-12)(biph)] [BArF4]** (3b). A solution of [Ir(CNC-12)(biph)] [BArF4] (1b) (45.7 mg, 30.0 μmol) in CH3Cl (ca. 1 mL) was freeze–pump–thaw degassed and placed under an atmosphere of CO to immediately afford a colorless solution. The volatiles were removed in vacuo, and the product recrystallized from CH2Cl2/hexane (1/15, ca. 15 mL) to afford the title compound as colorless blocks, which were isolated through decantation of the supernatant and dried in vacuo. Yields: 41.7 mg (85%).
and the structurally dynamic product quantitatively by 1H NMR in vacuo 95% yield, which was characterized in situ using 1H and 13C NMR. Isolated by filtration, washed with hexane (ca. 3 mL), and then dried in vacuo. Yield: 20.0 mg (69%, colorless foam).

A solution of [Rh(CNC-12)- (biph)][BAF4] (1a; 15.4 mg, 10.1 μmol) in CD2Cl2 (ca. 0.3 mL) was freeze–pump–thaw degassed and placed under an atmosphere of dihydrogen. After mixing for 6 h at ambient temperature, the resulting pale yellow solution was freeze–pump–thaw degassed and placed under an atmosphere of carbon monoxide to afford a yellow solution and the structurally dynamic product quantitatively by 1H NMR spectroscopy. Removal of volatiles in vacuo and redissolution in CD2Cl2 gave the static product by 1H NMR spectroscopy: data are consistent with the published values.6

1H NMR (500 MHz, CD2Cl2) signals for biphényle omitted: δ 7.88 (t, JFC = 7.8, 1H, py), 7.71–7.75 (m, 4H, ArF), 7.56 (br, 4H, ArF), 7.54 (d, JFC = 7.3, 2H, py), 7.13 (br, 2H, NCH), 7.00 (br, 2H, NCH), 5.09 (br, 4H, pyCH2), 4.02 (br, 4H, NCH), 1.72–1.86 (m, 4H, CH2), 1.26–1.54 (m, 16H, CH2), −9.46 (br, fwhm = 230 Hz, T1 = 94 ± 5 ms, 4H, IrH). 1H NMR (500 MHz, CD2Cl2/H2, 200 K, selected data): δ −9.56, (br, fwhm = 50 Hz, T1 = 29 ± 3 ms, 4H, IrH).13C(1H) NMR (126 MHz, CD2Cl2/H2, signals for biphényle omitted): δ 162.3 (q, JFC = 50, ArF), 156.8 (s, py), 134.1 (s, py), 134.3 (s, ArF), 129.4 (qq, JFC = 32, JFC = 3, ArF), 125.3 (s, py), 125.2 (q, JFC = 272, ArF), 121.9 (s, NCH), 120.9 (s, NCH), 118.1 (sept, JFC = 4, ArF), 59.5 (s, pyCH2), 52.3 (s, NCH), 30.3 (s, CH2), 27.8 (s, CH2), 27.6 (s, CH2), 26.9 (s, CH2), 25.5 (s, CH2). IR (CH2Cl2): ν(CO) 1978 cm−1. LR ESI-MS (positive ion): m/z 536.2 [M]+, calculated 536.2 m/z.

A solution of [Ir(CNC-12)H2(CO)][BAF4] (2b). A solution of [Ir(CNC-12) (biph)][BAF4] (1b; 32 mg, 20.0 μmol) in CD2Cl2 (ca. 0.5 mL) inside a J. Young valve NMR tube was freeze–pump–thaw degassed and placed under an atmosphere of dihydrogen. The solution was mixed for 24 h at ambient temperature to afford the product in ca. 95% yield, which was characterized in situ using 1H and 13C NMR spectroscopy.

1H NMR (500 MHz, CH2Cl2/H2, 200 K, selected data): δ 7.88 (t, JFC = 7.7, 1H, py), 7.71–7.75 (m, 8H, ArF), 7.56 (br, 4H, ArF), 5.29 (d, JFC = 14.7, 2H, pyCH2), 5.03 (d, JFC = 14.7, 2H, pyCH2), 4.29 (br, 2H, NCH), 3.98 (br, 2H, IR). CH2Cl2): ν(CO) 1978 cm−1. LR ESI-MS (positive ion): m/z 523 [M]+, calculated 523 m/z.

A solution of [Rh(CNC-12)-(biph)][BAF4] (1a; 31.2 mg, 19.3 μmol) in CH2Cl2 (ca. 1 mL) was freeze–pump–thaw degassed and placed under an atmosphere of carbon monoxide. Subsequent removal of volatiles in vacuo and redissolution in CD2Cl2 gave the static product by 1H NMR spectroscopy. Removal of volatiles in vacuo and redissolution in CD2Cl2 gave the static product by 1H NMR spectroscopy: data are consistent with the published values.6

1H NMR (500 MHz, CD2Cl2) signals for biphényle omitted: δ 7.89 (t, JHC = 7.8, 1H, py), 7.71–7.75 (m, 8H, ArF), 7.56 (br, 4H, ArF), 5.29 (d, JHC = 14.7, 2H, pyCH2), 5.03 (d, JHC = 14.7, 2H, pyCH2), 4.29 (br, 2H, NCH), 3.98 (br, 2H, IR). CH2Cl2): ν(CO) 1978 cm−1. LR ESI-MS (positive ion): m/z 523 [M]+, calculated 523 m/z.

A solution of [Ir(CNC-12)-H2][BAF4] (1b; 31.2 mg, 19.3 μmol) in CH2Cl2 (ca. 1 mL) was freeze–pump–thaw degassed and placed under an atmosphere of dihydrogen. The solution was mixed for 24 h at ambient temperature to afford the product in ca. 95% yield, which was characterized in situ using 1H and 13C NMR spectroscopy.

1H NMR (500 MHz, CH2Cl2/H2, 200 K, selected data): δ 7.89 (t, JHC = 7.8, 1H, py), 7.71–7.75 (m, 8H, ArF), 7.56 (br, 4H, ArF), 5.29 (d, JHC = 14.7, 2H, pyCH2), 5.03 (d, JHC = 14.7, 2H, pyCH2), 4.29 (br, 2H, NCH), 3.98 (br, 2H, IR). CH2Cl2): ν(CO) 1978 cm−1. LR ESI-MS (positive ion): m/z 523 [M]+, calculated 523 m/z.

A solution of [Rh(CNC-12)-(biph)][BAF4] (1b; 31.2 mg, 20.0 μmol) in CD2Cl2 (ca. 0.5 mL) inside a J. Young valve NMR tube was freeze–pump–thaw degassed and placed under an atmosphere of dihydrogen. The solution was mixed for 24 h at ambient temperature to afford the product in ca. 95% yield, which was characterized in situ using 1H and 13C NMR spectroscopy. Removal of volatiles in vacuo and redissolution in CD2Cl2 gave the static product by 1H NMR spectroscopy: data are consistent with the published values.6

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A solution of [Rh(CNC-12)-(biph)][BAF4] (1b; 31.2 mg, 20.0 μmol) in CD2Cl2 (ca. 0.5 mL) inside a J. Young valve NMR tube was freeze–pump–thaw degassed and placed under an atmosphere of dihydrogen. The solution was mixed for 24 h at ambient temperature to afford the product in ca. 95% yield, which was characterized in situ using 1H and 13C NMR spectroscopy.

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