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Article

## Synthesis and Reactivity of Zr MOFs Assembled from P<sup>N</sup>N<sup>N</sup>P-Ru **Pincer Complexes**

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S Supporting Information

**ABSTRACT:** Three isostructural Zr metal-organic frameworks have been synthesized from P<sup>N</sup>N<sup>N</sup>P-Ru pincer metallolinkers bearing different combinations of ancillary ligands  $(1, Zr_6O_4(OH)_4( OAc)_4 \{ cis - (P^N N^N P) RuCl_2(CO) \}_2; 2, Zr_6O_4(OH)_4(O_2CH)_4 \}$  $\{(P^NN^NP)RuCl(CO)_2\}_2Cl_2; 3, Zr_6O_4(OH)_4(OAc)_4\{cis-/trans (P^{N}N^{N}P)RuCl_{2}(CO)$ <sub>2</sub>;  $P^{N}N^{N}P = 2,6-(HNPAr_{2})_{2}C_{5}H_{3}N$ ; Ar = p- $C_6H_4CO_2^{-}$ ). The structure and composition of the  $P^NN^NP$ -Ru pincer MOFs have been determined using synchrotron X-ray powder diffraction, solid- and solution-state NMR spectroscopy, IR spectroscopy, and elemental analysis. Reaction of 2 with KO<sup>t</sup>Bu results in deprotonation of an NH group of the P<sup>N</sup>N<sup>N</sup>P-RuCl(CO)<sub>2</sub> linkers. Subsequent treatment with Me<sub>3</sub>NO removes a Ru-coordinated CO ligand, generating 2-b, which proved to be a recyclable catalyst for the



hydrosilylation of aryl aldehydes with Et<sub>3</sub>SiH. A similar postsynthetic treatment of 1 and 3 does not generate active catalysts, highlighting the importance of precatalyst design and activation. A homogeneous analogue of 2-b also showed inferior catalytic performance, demonstrating the benefit of catalyst immobilization.

#### INTRODUCTION

Metal-organic frameworks (MOFs) have attracted considerable interest as supports for heterogeneous catalysis owing to their tunable structures, porosity, and chemical functionality.1-8 The use of well-defined molecular building blocks for MOF assembly can amalgamate the beneficial traits of homogeneous and heterogeneous catalyst systems. In addition, MOFs offer a platform to explore site isolation or secondary environment effects on the catalytic activity and selectivity of a catalyst. A diverse range of strategies, including encapsulation, activation of metal nodes, postsynthetic grafting, and direct assembly, have been used to functionalize MOFs with catalytically active transition-metal species.<sup>9-22</sup> However, further postsynthetic steps are still often necessary to activate MOF-supported precatalysts. In some cases, desolvation carried out by heating a MOF in vacuo can remove bound solvent molecules, generating coordinatively unsaturated metal sites for Lewis acid-catalyzed transformations.<sup>23-27</sup> In other cases, one or more reagent may be required to facilitate precatalyst activation via X-type ligand exchange or abstraction, similar to procedures commonly employed for homogeneous organometallic complexes.<sup>28-32</sup> For example, reagents such as silver salts of weakly coordinating anions have been used to exchange metal-coordinated halide ligands in MOFs and organoaluminum or organolithium reagents have been employed to activate metal nodes for olefin oligomerization catalysis.<sup>33–37</sup> Careful consideration of precatalyst activation

procedures is perhaps more important for MOF-based catalysts than for homogeneous systems. First of all, the strategies used to introduce a catalytic functionality may rely on transitionmetal species with muted reactivity to prevent decomposition or undesirable side reactions during incorporation. Second, MOFs and other heterogeneous supports may give rise to reagent compatibility issues that are not encountered with homogeneous systems. For example, strong acids or bases may lead to framework degradation.<sup>38,39</sup> In our own experience, halide ligand abstraction with silver salts has not proven to be particularly effective with MOFs, in part due to the precipitation of insoluble silver halide byproducts that are inseparable from the heterogeneous catalyst.<sup>40</sup>

Our group and others have been interested in the design and study of MOFs containing diphosphine pincer complexes.<sup>40–47</sup> Diphosphine pincer ligands have been employed for a wide range of homogeneous catalytic transformations.<sup>48-57</sup> They offer a great deal of electronic and steric diversity as well as chemical and thermal stability and have been shown to support catalytically active complexes with nearly all mid-to-late transition metals. Consequently, the diphosphine pincer ligand

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architecture represents an epitomic platform for the design and study of a general class of MOF catalysts with the potential for broad scope catalytic activity.

Herein we report the synthesis, characterization, and preliminary investigation of the reactivity and catalytic activity of an isostructural series of Zr MOFs (1-3) assembled from P<sup>N</sup>N<sup>N</sup>P-Ru pincer complexes. The new MOFs have been synthesized from P<sup>N</sup>N<sup>N</sup>P-Ru linker precursors containing different ancillary ligands (chloride, CO, or phosphines). Despite these differences, solvothermal reactions with ZrCl<sub>4</sub> converge to an isostructural series of MOFs that adopt a csqtype net and are similar to a recently reported Zr MOF assembled from P<sup>N</sup>N<sup>N</sup>P-Co(III) linkers.<sup>47</sup> Homogeneous Ru diphosphine pincer complexes have been widely studied as catalysts for dehydrogenation, transfer, and direct hydro-genation of organic transformations.<sup>51,58</sup> For many of these reactions, ligand-based deprotonation is necessary to activate the Ru diphosphine pincer complexes, and subsequent metalligand cooperativity has been proposed to facilitate key steps in catalytic cycles.<sup>57,59,60</sup> We find that deprotonation followed by CO ligand removal with Me<sub>3</sub>NO serves to activate 2 for the catalytic hydrosilylation of aldehydes with Et<sub>3</sub>SiH. The other members of the P<sup>N</sup>N<sup>N</sup>P-Ru MOF series as well as homogeneous analogues of the immobilized pincer complexes show low activity for the hydrosilylation reaction under similar precatalyst activation conditions.

#### RESULTS AND DISCUSSION

Synthesis of  $P^NN^P$ -Ru Complexes. The carboxylatefunctionalized  $P^NN^NP$  pincer ligand  ${}^tBu_4L$  was synthesized as previously described and used to prepare the series of Ru complexes shown in Scheme 1.<sup>40</sup> All of the new complexes





"Reagents and conditions: (i)  $RuCl(H)(CO)(PPh_3)_3$ , THF, 70 °C, 16 h; (ii)  $NaO_2CCF_3$ , THF/CHCl<sub>3</sub>, room temperature, 2 h; (iii) CF<sub>3</sub>CO<sub>2</sub>H, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 16 h; (iv)  $RuCl_2(CO)_3(THF)$ , 1,4-dioxane, 100 °C, 16 h; (v) Me<sub>3</sub>NO, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 1 h.

have been characterized by multinuclear NMR and IR spectroscopy and elemental analysis (Figures S1–S20). The *cis* stereochemistry of [<sup>t</sup>Bu<sub>4</sub>L-RuCl(CO)<sub>2</sub>]Cl and [H<sub>4</sub>L-RuCl(CO)<sub>2</sub>]TFA is established by the presence of two distinct sets of aromatic <sup>1</sup>H NMR resonances corresponding to inequivalent benzoate groups as well as two carbonyl stretching bands of equal intensity appearing at 2064 and 2010 cm<sup>-1</sup> in the

ATR-IR spectrum. These spectroscopic features are in line with an analogous PNP-Ru pincer complex reported by Mashuta and co-workers.<sup>61</sup> Treatment of *cis*-[<sup>t</sup>Bu<sub>4</sub>L-RuCl-(CO)<sub>2</sub>]Cl with a mild oxidative decarbonylating agent, Me<sub>3</sub>NO, facilitates loss of a CO ligand, and subsequent deprotection gives H<sub>4</sub>L-RuCl<sub>2</sub>(CO).<sup>62</sup> The <sup>1</sup>H and <sup>31</sup>P NMR spectra of the product indicates a ~1:3 mixture of cis and trans isomers.

Synthesis and Characterization of  $P^NN^P-Ru$  MOFs. Solvothermal reactions of  $[H_4L-Ru(TFA)(CO)(PPh_3)]TFA$ ,  $[H_4L-RuCl(CO)_2]TFA$ , and *cis/trans*-H<sub>4</sub>L-RuCl<sub>2</sub>(CO) with ZrCl<sub>4</sub> in DMF using CH<sub>3</sub>CO<sub>2</sub>H or HCO<sub>2</sub>H as modulators yields an isostructural series of MOFs, 1–3, as off-white microcrystalline powders (Scheme 2). Although 2 could be





synthesized using  $CH_3CO_2H$  as a modulator, we found that  $HCO_2H$  provides a more crystalline product. X-ray powder diffraction (XRPD) analysis indicates that **1–3** adopt csq-type frameworks that are analogous to a recently reported Zr MOF assembled from  $P^NN^PP-CoCl_3$  metallolinkers (Figure 1a).<sup>47</sup>

The framework structure of 1 was interrogated by Rietveld refinement of synchrotron X-ray powder diffraction (SXPD) data. Initial indexing provided a hexagonal unit cell (a =31.937(7) Å, c = 15.798(4) Å), and a structure model was constructed with P6/mmm space group symmetry on the basis of the structure of the reported P<sup>N</sup>N<sup>N</sup>P-CoCl<sub>3</sub> framework.<sup>47</sup> Rietveld refinement was carried out using simulated annealing with a  $[Zr_6O_4(OH)_4(OAc)_4]^{8+}$  metal cluster and an idealized [L-RuCl<sub>3</sub>]<sup>4-</sup> linker as rigid bodies. Although the metallolinker in 1 was identified as  $[cis-L-RuCl_2(CO)]^{4-}$  on the basis of NMR and IR spectroscopic data (vide infra), the CO ligand was approximated by a nearly isoelectronic chloride group in the rigid body to maintain space group symmetry and simplify the Rietveld refinement. The refinement converged to  $R_{wp}$  = 14.03 with final lattice parameters of a = 31.9437(6) Å and c =15.8051(3) Å. The refined structure of 1 shows small trigonal and larger hexagonal channels along the c axis (Figure 1c). The large channels have a maximum diameter of ~15 Å but are constricted to a minimum diameter of ~6 Å by the inwardfacing arene groups of the pincer complexes. The mean plane of the pincer arene groups is oriented perpendicular to the crystallographic ab plane. The [cis-L-RuCl<sub>2</sub>(CO)]<sup>4-</sup> linkers and OAc groups of the  $[Zr_6O_4(OH)_4(OAc)_4]^{8+}$  metal clusters face inward to the smaller trigonal channels, restricting their diameter to ~6 Å.

Solution- and solid-state NMR spectroscopy has been used to determine the composition of 1-3. The solid-state <sup>31</sup>P NMR spectrum of 1 shows a single major resonance centered



**Figure 1.** (a) XRPD patterns (Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å) for 1– 3. (b) Rietveld refinement profile of 1 from SXPD data ( $\lambda = 0.414536$  Å). (c) Framework structure of 1. (d) Structure of the  $D_{4h}$  [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OAc)<sub>4</sub>]<sup>8+</sup> secondary building units.

at 68 ppm, and no signal attributable to the PPh<sub>3</sub> ligand was observed (Figure 2). This finding is corroborated by solutionstate NMR analysis of a CsF-digested sample, which shows one major singlet resonance at 70.6 ppm in the <sup>31</sup>P NMR spectrum and a set of signals in the  ${}^{1}\overline{H}$  NMR spectrum that are consistent with a single  $P^N N^N P$ -Ru complex exhibiting  $C_s$ symmetry (Figures S22 and S23). The ATR-IR spectrum of 1 shows a broad Ru–CO stretching band at 1982 cm<sup>-1</sup> (Figure S41). Overall, the spectroscopic data are consistent with *cis*-[L- $RuCl_2(CO)$ ]<sup>4-</sup> linkers resulting from substitution of the Ph<sub>3</sub>P and TFA ancillary ligands in [H<sub>4</sub>L-Ru(TFA)(CO)(PPh<sub>3</sub>)] with Cl<sup>-</sup> during the solvothermal assembly. Accordingly, <sup>31</sup>P NMR analysis of the supernatant solution from the solvothermal synthesis shows the presence of Ph<sub>3</sub>PO (Figure S26). The <sup>1</sup>H NMR spectrum of a CsF-digested sample of 1 also shows that  $CH_3CO_2H$  is present in a ~2:1 ratio with respect to the  $P^N N^N P$ -RuCl<sub>2</sub>(CO) metallolinkers, supporting the presence of  $[Zr_6O_4(OH)_4(OAc)_4]^{8+}$  secondary building units (SBUs) in the MOF (Figure S23); the bound acetate is also detected in the <sup>13</sup>C NMR spectrum of the MOF (Figure S27d).



Figure 2. Solid-state  ${}^{31}$ P NMR spectra of 1, 2, and 3. Asterisks (\*) mark residual spinning side bands.

The solid-state and acid-digested, solution-state <sup>31</sup>P NMR spectra of **2** both exhibit a major resonance at 82 ppm, which is consistent with the presence of *cis*- $[H_4(L-RuCl(CO)_2)]^+$  pincer complexes (81.8 ppm in DMSO-*d*<sub>6</sub>). The solid-state <sup>13</sup>C NMR spectrum of the MOF and the <sup>1</sup>H NMR spectrum after acid digestion show all expected resonances for  $[H_4(L-RuCl(CO)_2)]^+$  as well as  $HCO_2H$  arising from  $[Zr_6O_4(OH)_4(O_2CH)_4]^{8+}$  SBUs (Figures S27e and S28). The ATR-IR spectrum of **2** contains two strong  $\nu(CO)$  bands of similar intensity at 2070 and 2016 cm<sup>-1</sup>, indicating that the two carbonyl ligands remain in a cis arrangement (Figure S41).

The solid-state <sup>31</sup>P NMR spectrum of 3 shows two major resonances at 68 and 92 ppm, corresponding to a ~1:2 mixture of cis- and trans-[L-RuCl<sub>2</sub>(CO)]<sup>4-</sup> linkers in the MOF. The minor resonance at 82 ppm matches that observed for 2, indicating that 3 contains a small amount (<10%) of cis-[L- $RuCl(CO)_2$ <sup>3-</sup> metallolinkers. This species is likely generated from CO produced as a result of DMF decomposition. Greater amounts of cis-[L-RuCl(CO)<sub>2</sub>]<sup>3-</sup> were observed when the solvothermal synthesis of 3 was carried out with longer reaction times or with HCO<sub>2</sub>H instead of CH<sub>3</sub>CO<sub>2</sub>H as the modulator (Figure S32), but its formation could be almost completely inhibited by limiting the solvothermal reaction times to 20 h. Under these conditions, the acid-digested <sup>31</sup>P NMR spectrum of 3 shows only resonances attributable to cisand trans-[L-RuCl<sub>2</sub>(CO)]<sup>4-</sup> complexes at 73.9 and 90.9 ppm, respectively, and a single  $\nu(CO)$  band at 1988 cm<sup>-1</sup> in the ATR-IR spectrum (Figures S22 and S41).

Thermogravimetric analyses (TGA) of MeOH-exchanged samples of 1 and 3 show the loss of guest solvent molecules ( $\sim$ 20 wt %) up to 100 °C and the onset of framework decomposition at 300–350 °C (Figures S33 and S34). XRPD

analysis revealed that 2 was unstable to drying after MeOH solvent exchange (Figure S36). As a result, THF was used for solvent exchange, although <sup>1</sup>H NMR analysis showed that it could not completely remove DMF guest solvent molecules. Subsequent TGA analysis of THF-exchanged 2 shows the loss of guest solvent molecules (~30 wt %) up to 200 °C and framework decomposition above 350 °C (Figure S35). N<sub>2</sub> adsorption isotherms (77 K) measured for samples of 1-3after solvent exchange and desolvation by heating at 100 °C and 10<sup>-4</sup> Torr for 16 h gave calculated BET surface areas of 928, 334, and 728 m<sup>2</sup> g<sup>-1</sup>, respectively (Figures S37-S39). Notably, the BET surface area of 1 is only slightly lower than the theoretical accessible surface area (1019 m<sup>2</sup> g<sup>-1</sup>) calculated using the structure model obtained from Rietveld refinement.<sup>63</sup> 2 showed a modest increase in N2 uptake and BET surface area  $(451 \text{ m}^2 \text{ g}^{-1})$  when the MOF was activated by lyophilization with benzene. However, XRPD analysis shows that, while 1 and 3 remain crystalline after activation, 2 experiences a loss of crystallinity (Figure S40). The poor structural stability of 2 may be due to a greater number of defects resulting from the use of HCO<sub>2</sub>H as a modulator.<sup>64</sup> The ATR-IR spectra of activated samples of 2 still show the presence of two  $\nu(CO)$ bands, indicating that desolvation does not lead to significant loss of Ru-coordinated CO ligands (Figure S42). <sup>1</sup>H and <sup>31</sup>P NMR analyses of acid-digested samples of desolvated 2 confirm that cis-[L-RuCl(CO)<sub>2</sub>]<sup>3-</sup> is the major linker component with only a small amount of [L-RuCl<sub>2</sub>(CO)]<sup>4-</sup> species resulting from CO ligand loss (Figures S29 and S30).

Postsynthetic Activation and Catalytic Hydrosilylation Studies. Deprotonation of the methylene or amide linker groups of Ru diphosphine pincer complexes has proven to be a valuable strategy for precatalyst activation.<sup>58–60,65</sup> The deprotonation step often eliminates coordinated halide ligands, increases the ligand donor strength of the central pyridine, and can switch on metal–ligand cooperativity in subsequent steps of a catalytic cycle. With this precedent in mind, we investigated a sequence of postsynthetic deprotonation and CO ligand removal steps as a means of activating 1-3 for further reactivity and catalytic studies.

The MOFs were treated with KO<sup>t</sup>Bu (2 equiv per Ru) in THF to induce deprotonation of the NH linker groups (Scheme 3). Subsequent XRPD analysis revealed reflections





<sup>a</sup>Reagents and conditions: (i) KO<sup>t</sup>Bu, THF, room temperature, 16 h; (ii) Me<sub>3</sub>NO, THF/CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 16 h.

attributable to crystalline KCl in 2-a, but not in the basetreated samples of 1 and 3 (Figure 3b and Figures S45–S47). The difference in reactivity observed for 2 is presumably due to the presence of outer-sphere Cl<sup>-</sup> ions that are more easily released than the inner-sphere halides found in 1 and 3. The ATR-IR spectrum of 2-a shows that the CO stretching bands are shifted to lower energy by ~20 cm<sup>-1</sup> in comparison to those observed for 2 (Figure 3a). This redshift is consistent with weakening of C $\equiv$ O bonds due to an increase in electron density at the Ru center.<sup>66</sup> The reaction of the homogeneous



**Figure 3.** (a) ATR-IR spectra for **2**, **2**-**a**, and **2**-**b**. (b) XRPD patterns (Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å) for **2**-**b** before catalysis and after catalytic run 4.

analogue, *cis*-[<sup>t</sup>Bu<sub>4</sub>L-RuCl(CO)<sub>2</sub>]Cl, with KO<sup>t</sup>Bu results in a similar shift in the CO stretching bands (Figure S48). The Ru sites in **2-a** remain coordinatively saturated owing to the presence of the two strongly bound CO ligands. Consequently, the MOF was treated with Me<sub>3</sub>NO to generate **2-b**. The loss of a CO ligand was confirmed by the appearance of a single broad CO stretching band at 1955 cm<sup>-1</sup> (Figure 3a).

Catalytic hydrosilylation of carbonyls provides a mild and economical route for generating silane-protected alcohols. Homogeneous organometallic complexes, including those supported by diphosphine pincer ligands, have been reported to efficiently catalyze the hydrosilylation of carbonyl groups.<sup>67-71</sup> However, relatively few MOFs have been reported to catalyze hydrosilylation reactions.<sup>72-75</sup> Hydrosilvlation of carbonyls with a well-defined and recyclable catalyst presents an attractive approach to the hydrogenation of carbonyl substrates. Consequently, we set out to examine the P<sup>N</sup>N<sup>N</sup>P-Ru MOFs as catalysts for the hydrosilylation of aldehydes and ketones. Initial catalytic reactions were carried out at 100 °C in 1,4-dioxane with benzaldehyde and Et<sub>3</sub>SiH as substrates and 5 mol % catalyst loading (based on Ru). Product yields were determined by <sup>1</sup>H NMR and/or GC-MS/ FID analysis with hexamethylbenzene as an internal standard. The unactivated MOFs 1-3 afforded less than 6% yield of benzyloxytriethylsilane under these conditions (Table 1, entries 1, 3, and 6).

In contrast, **2-b** proved to be an effective catalyst, providing the silyl ether product in 94% yield after 12 h (entry 5). The deprotonated MOF **2-a** (10% yield) and a sample of **2** treated with Me<sub>3</sub>NO (6% yield, Figure S54) showed little activity for

Table 1. Catalytic Hydrosilylation of Benzaldehyde<sup>a</sup>

	O + Et₃SiH ( 2 equiv.)	_OSiEt <sub>3</sub>
entry	catalyst	yield (%) <sup>b</sup>
1	1	<5
2	1-KO <sup>t</sup> Bu	<5
3	2	<5
4	2-a	10
5	2-b	94
6	3	6
7	3-KO <sup>t</sup> Bu	<5
8	[ <sup>t</sup> Bu <sub>4</sub> L-RuCl(CO) <sub>2</sub> ]Cl	<5
9	<sup>t</sup> Bu <sub>4</sub> L-RuCl <sub>2</sub> (CO)	<5
10	[ <sup>t</sup> Bu <sub>4</sub> L-RuCl(CO) <sub>2</sub> ]Cl/KO <sup>t</sup> Bu/Me <sub>3</sub> NO <sup>c</sup>	10
11	<b>2-b</b> (run 2)	33
12 <sup>d</sup>	<b>2-b</b> (run 3)	95
13 <sup>d</sup>	<b>2-b</b> (run 4)	72

<sup>*a*</sup>Reaction conditions: substrate (0.2 mmol), catalyst (0.01 mmol), silane (0.4 mmol), dioxane (1 mL), 12 h, 100 °C. <sup>*b*</sup>Yields were determined by <sup>1</sup>H NMR spectroscopy with respect to an internal standard (hexamethylbenzene). <sup>*c*1</sup>Bu<sub>4</sub>L-RuCl(CO)<sub>2</sub>]Cl treated with KO<sup>t</sup>Bu followed by Me<sub>3</sub>NO. <sup>*d*</sup>The catalyst was regenerated by treatment with Me<sub>3</sub>NO.

the reaction. These results support catalysis occurring at the activated Ru sites rather than Lewis acidic Zr sites and highlight the importance of the deprotonation and CO ligand removal steps for precatalyst activation. Recent work by Huang and co-workers suggests that a deprotonated P<sup>N</sup>N<sup>N</sup>P-NiH complex may act as a basic "organocatalyst" in hydrosilylation reactions without direct involvement of the Ni center.<sup>76</sup> While we cannot rule out the possibility of a related mechanism for 2-b, the need for CO ligand removal implies the requirement of a coordinatively unsaturated Ru center. The catalytic efficiency of 2-b dropped considerably (33% yield) upon attempted recycling of the catalyst. The ATR-IR spectrum of the MOF after the second run showed the appearance of new CO stretching bands at 2050 and 1980 cm<sup>-1</sup>, consistent with the formation of cis-[L-RuCl(CO)<sub>2</sub>]<sup>3-</sup> pincer species (Figure S49). The appearance of cis-[L- $\operatorname{RuCl}(\operatorname{CO}_2)^{3-}$  can be attributed to off-cycle decarbonylation of benzaldehyde and, on the basis of the poor catalytic activity of 2 and 2-a, should lead to catalyst deactivation. Notably, 2-b was not observed to catalyze decarbonylation of benzaldehyde at elevated temperatures or in the presence of Me<sub>3</sub>NO as a CO scavenger. Nevertheless, we found that the recovered MOF catalyst could be reactivated for subsequent hydrosilylation reactions upon treatment with Me<sub>3</sub>NO. The ensuing catalytic run (entry 12) showed nearly complete recovery of the catalytic activity, although a modest drop in activity was observed in subsequent recycling steps.

Notably, 2-b remains crystalline after regenerating and recycling the catalyst (Figure 3b). Moreover, no additional substrate conversion was observed in the reaction supernatant after hot filtration, supporting the heterogeneous nature of the catalysis (Figure S62). 2-b demonstrates good catalytic activity for hydrosilylation of a range of benzaldehyde derivatives (Table S3). However, <10% yield of hydrosilylated product was obtained with a large substrate, 3,5-dibenzyloxybenzaldehyde, indicating substrate transport limitations within the

MOF (Figures S71 and S72). **2-b** also shows unexpectedly low catalytic activity with acetophenone as a substrate.

The homogeneous complexes  $[^{t}Bu_{4}L-RuCl(CO)_{2}]Cl$  and <sup>t</sup>Bu<sub>4</sub>L-RuCl<sub>2</sub>(CO) were found to be inactive for the catalytic hydrosilvlation reaction (Table 1, entries 8 and 9), and a homogeneous analogue of 2-b prepared by treating [<sup>t</sup>Bu<sub>4</sub>L- $RuCl(CO)_2$  Cl with KO<sup>t</sup>Bu and Me<sub>3</sub>NO showed only a slight increase in catalytic activity (entry 10). Interestingly, NMR analysis of  $[{}^t\!Bu_4L\text{-}RuCl(CO)_2]Cl$  after the deprotonation and CO ligand removal steps showed a mixture of species that could not be clearly identified but give rise to signals characteristic of P<sup>N</sup>N<sup>Ń</sup>P-Ru complexes. The ATR-IR spectrum of the activated homogeneous complex also shows a single broad CO stretching band at 1951 cm<sup>-1</sup>, confirming formation of monocarbonyl species resembling that observed in 2-b (Figure S48). Attempts to isolate and further characterize these species were unsuccessful. <sup>31</sup>P NMR analysis of the homogeneous reaction mixture after catalysis shows a similarly complex mixture of species, but no signals indicative of pincer decomposition were observed. Although it is not presently clear why the homogeneous P<sup>N</sup>N<sup>N</sup>P-Ru complexes are inactive for catalytic hydrosilylation, their immobilization as linkers in 2-b proves to be beneficial for stabilizing catalytically active species.

#### CONCLUSIONS

In summary, we have described the synthesis, characterization, and reactivity of a series of three isostructural Zr MOFs assembled from P<sup>N</sup>N<sup>N</sup>P-Ru metallolinkers. Among these MOFs, only 2 could be readily activated to generate a heterogeneous catalyst for the hydrosilylation of aryl aldehydes. The difference in reactivity among the series is rationalized by the presence of outer-sphere Cl<sup>-</sup> ions in 2 that are more readily eliminated than the coordinated Cl ligands in 1 and 3. Subsequent CO-ligand removal from 2-a generates a coordinatively unsaturated P<sup>N</sup>N<sup>N</sup>P-Ru species capable of catalyzing hydrosilylation reactions. These results demonstrate the importance of the rational and diligent activation of MOF precatalysts. Moreover, the disparate reactivity of 2 and its homogeneous analogue point to a beneficial site isolation effect. Ongoing studies are focused on elucidating the origin of this effect and expanding the catalytic applications of MOF-immobilized  $P^N N^N P$ -Ru pincer complexes.

#### EXPERIMENTAL SECTION

General Considerations. <sup>t</sup>Bu<sub>4</sub>(L)<sup>40</sup> and RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub><sup>78</sup> were prepared following literature procedures. THF and 1,4-dioxane were degassed by sparging with ultrahigh-purity argon and dried via passage through columns of drying agents using a solvent purification system from Pure Process Technologies. All other solvents and reagents were purchased from commercial suppliers and used as received. Routine X-ray powder diffraction (XRPD) patterns for phase identification were collected using a Rigaku Miniflex 600 diffractometer with nickel-filtered Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). High-resolution synchrotron X-ray powder diffraction (SXPD) data were collected at 295 K using beamline 11-BM at the Advanced Photon Source (APS, Argonne National Laboratory, Argonne, IL) with an average wavelength of 0.414536 Å. Rietveld refinement was carried out with TOPAS-Academic.<sup>79</sup> ATR-IR spectra were measured using a Bruker Alpha II spectrometer with a diamond ATR accessory. N<sub>2</sub> adsorption isotherms (77 K, liquid nitrogen bath) were measured using a Micromeritics 3Flex Surface Characterization Analyzer. Prior to analysis, samples (100-200 mg) were heated under reduced pressure until the outgas rate was less than 2 mTorr/min. GC-MS

analysis was performed using an Agilent 7890B GC system equipped with the HP-5 Ultra Inert column (30 m, 0.25 mm, 0.25  $\mu$ m) and an FID detector. For MS detection an electron ionization system was used with an ionization energy of 70 eV. Elemental analyses (C, H, N) were performed by Robertson Microlit Laboratories (Ledgewood, NJ).

Solution-state NMR spectra were measured using either a Varian Inova or Bruker 400 MHz spectrometer. For <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the solvent resonance was referenced as an internal standard. For <sup>31</sup>P NMR spectra, 85% H<sub>3</sub>PO<sub>4</sub> was used as an external standard (0 ppm). Solvent-suppressed <sup>1</sup>H NMR spectra were collected using 180° water selective excitation sculpting with default parameters and pulse shapes.<sup>80</sup> Solid-state NMR experiments were performed using a Bruker DSX-400 spectrometer at a resonance frequency of 162 MHz for <sup>31</sup>P with a magic-angle spinning (MAS) probe in double-resonance mode. Samples were packed into 4 mm rotors with Kel-F 22  $\mu$ L HRMAS inserts. Experiments were carried out at spinning frequencies of 10–13.5 kHz. Typical <sup>31</sup>P and <sup>1</sup>H 90° pulse lengths were 4 and 6  $\mu$ s, respectively. <sup>31</sup>P NMR spectra were obtained after compositepulse multiple cross-polarization from <sup>1</sup>H, with a recycle delay of 1 s and 10 blocks of 1.1 ms 90-100% ramp cross-polarization separated by 0.5 s <sup>1</sup>H repolarization periods.<sup>81</sup> Four-pulse total suppression of sidebands (TOSS) was used to obtain spectra almost without spinning sidebands.<sup>82</sup> Two-pulse phase modulation <sup>1</sup>H decoupling was applied during detection.<sup>83 31</sup>P spectra were externally referenced to the upfield resonance of calcium hydroxyapatite (National Institute of Standards and Technology) at 2.73 ppm; this corresponds to the 85% H<sub>3</sub>PO<sub>4</sub> scale.

**Synthesis of** [<sup>t</sup>Bu<sub>4</sub>L-RuH(CO)(PPh<sub>3</sub>)]Cl. A solution of <sup>t</sup>Bu<sub>4</sub>(L) (0.77 g, 0.88 mmol) in THF (3 mL) was added dropwise to a suspension of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (0.84 g, 0.88 mmol) in THF (20 mL). The reaction was heated at 60 °C overnight with vigorous stirring, resulting in formation of a white precipitate. After it was cooled to room temperature, the solid was collected by filtration, washed with Et<sub>2</sub>O (3 × 10 mL), and dried in vacuo to afford a white powder (0.84 g, 73%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  –7.24 (dt, 1H, <sup>2</sup>*J*<sub>P-H</sub> = 86.88 Hz, 26.23 Hz, Ru-H), 1.53 (s, 36H, tBu), 6.26 (d, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 8.26 Hz, pyridine Ar-H), 6.98 (m, 15H, PPh<sub>3</sub> Ar-H), 7.28 (m, 5H, pyridine and benzoate Ar-H), 7.60 (d, 4H, <sup>3</sup>*J*<sub>H-H</sub> = 8.15 Hz, benzoate Ar-H), 8.06 (m, 8H, benzoate Ar-H), 9.94 (br, 2H, NH). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  39.8 (t, 1P, <sup>2</sup>*J*<sub>P-P</sub> = 18.69 Hz), 99.9 (d, 2P, <sup>2</sup>*J*<sub>P-P</sub> = 19.31 Hz). ATR-IR: ν(CO) 1940 cm<sup>-1</sup>. Anal. Calcd for [<sup>t</sup>Bu<sub>4</sub>(LRuH)]Cl·H<sub>2</sub>O, C<sub>68</sub>H<sub>75</sub>ClN<sub>3</sub>O<sub>10</sub>P<sub>3</sub>Ru: C, 61.70; H, 5.71; N, 3.17. Found: C, 61.30; H, 5.47; N, 3.13.

Synthesis of [<sup>t</sup>Bu<sub>4</sub>L-RuH(CO)(PPh<sub>3</sub>)]TFA. A solution of NaO<sub>2</sub>CCF<sub>3</sub> (0.14 g, 0.96 mmol) in THF (5 mL) was added to a solution of  $[{}^tBu_4L\mbox{-}RuH(CO)(PPh_3)]Cl\ (0.92\ g,\ 0.70\ mmol)$  in CHCl<sub>3</sub> (5 mL) and stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the solid was extracted into CHCl<sub>2</sub> (5 mL) with sonication. The resulting suspension was filtered through a pad of Celite to ensure complete removal of NaCl. After the solvent was removed in vacuo, the product was obtained as a gray powder (0.90 g, 93%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  -7.35  $(dt, 1H, {}^{2}J_{P-H} = 86.57 Hz, 23.35 Hz, Ru-H), 1.52 (s, 36H, tBu), 6.23$ (d, 2H,  ${}^{3}J_{H-H} = 7.24$  Hz, pyridine Ar-H), 6.99 (m, 15H, PPh<sub>3</sub> Ar-H), 7.28 (br, 5H, pyridine and benzoate Ar-H), 7.60 (d, 4H,  ${}^{3}J_{H-H} = 7.63$ Hz, benzoate Ar-H), 8.06 (br, 8H, benzoate Ar-H), 9.90 (br, 2H, NH). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DMSO- $d_6$ ):  $\delta$  39.8 (t, 1P, <sup>2</sup> $J_{P-P}$  = 19.75 Hz), 99.8 (d, 2P,  ${}^{2}J_{P-P}$  = 19.26 Hz). ATR-IR:  $\nu$ (CO) 1945  $\mathrm{cm}^{-1}$ 

Synthesis of [H<sub>4</sub>L-Ru(TFA)(CO)(PPh<sub>3</sub>)]TFA. A 20 mL scintillation vial was charged with [<sup>t</sup>Bu<sub>4</sub>L-RuH(CO)(PPh<sub>3</sub>)]TFA (0.90 g, 0.60 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), and CF<sub>3</sub>CO<sub>2</sub>H (1 mL) and stirred at room temperature for 16 h. The solvent was then removed using a rotary evaporator, and the resulting brown solid was dissolved in a minimal amount of methanol (~2 mL). The product was precipitated with Et<sub>2</sub>O (~15 mL), collected by filtration, and washed with Et<sub>2</sub>O (3 × 10 mL). The product was obtained as a white powder (0.66 g, 87%) after drying in vacuo. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  6.67 (d, 2H, <sup>3</sup>*J*<sub>H-H=</sub> 7.76 Hz, pyridine Ar-H), 7.08 (m, 12H, PPh<sub>3</sub> Ar-H), 7.24 (t, 8H,  ${}^{3}J_{H-H} = 6.00$  Hz, benzoate Ar-H), 7.39 (br, 3H, PPh<sub>3</sub> Ar-H), 7.73 (t, 1H,  ${}^{3}J_{H-H} = 8.23$  Hz, pyridine Ar-H), 7.79 (d, 4H,  ${}^{3}J_{H-H} = 7.86$  Hz, benzoate Ar-H), 7.95 (d, 4H,  ${}^{3}J_{H-H} = 7.86$  Hz, benzoate Ar-H), 7.95 (d, 4H,  ${}^{3}J_{H-H} = 7.86$  Hz, benzoate Ar-H),  ${}^{31}P{}^{1}H$  NMR (162 MHz, DMSO- $d_{6}$ ):  $\delta$  27.6 (t, 1P,  ${}^{2}J_{P-P} = 24.3$  Hz), 78.1 (d, 2P,  ${}^{2}J_{P-P} = 22.68$  Hz). ATR-IR:  $\nu$ (CO) 1982 cm<sup>-1</sup>. Anal. Calcd for [H<sub>4</sub>L-Ru(TFA)(CO)(PPh<sub>3</sub>)]TFA, C<sub>56</sub>H<sub>40</sub>F<sub>6</sub>N<sub>3</sub>O<sub>13</sub>P<sub>3</sub>Ru: C, 52.92; H, 3.17; N, 3.31. Found: C, 53.44; H, 3.47; N, 3.47; N, 3.42.

Synthesis of 1. A 20 mL scintillation vial was charged with ZrCl<sub>4</sub> (16 mg, 0.070 mmol), DMF (4 mL), and glacial acetic acid (1.5 mL). The mixture was sonicated for 20 min until it became a clear colorless solution. The solution was then transferred to a vial containing a solution of [H<sub>4</sub>L-Ru(TFA)(CO)(PPh<sub>3</sub>)]TFA (30 mg, 0.024 mmol) in DMF (2 mL). The vial was sealed with a Teflon-lined screw-top cap (Qorpak CAP-00554) and heated to 120 °C in a programmable oven for 16 h. After the reaction mixture was cooled to room temperature, the solid was collected by centrifugation, washed with DMF ( $3 \times 10$  mL), and soaked in MeOH ( $4 \times 10$  mL) for a total of 24 h. 1 was obtained as a nearly colorless microcrystalline powder (40 mg) after drying in vacuo.  ${}^{31}P{}^{1}H$  NMR (162 MHz, CsF/DMSO- $d_6$ /  $D_2O$ :  $\delta$  70.8 (s, 2P), 28.5 (broad, minor impurity). On the basis of elemental analysis and NMR spectroscopic data obtained for 1 after MeOH solvent exchange and activation (Figures S23-S25), the empirical formula is best given as  $Zr_6O_4(OH)_4(CH_3CO_2)_{2.8}(OH)_{0.4}$  $(L-RuCl_2(CO))_2(Ar_2PO_2Me)_{0.4}(MeOH)_{0.15}(DMF)_{0.5}$  (Ar =  $p-C_6H_4$ - $CO_2$ ). The presence of  $Ar_2PO_2Me$  in 1 is supported by the minor resonance observed in solid- and solution-state <sup>31</sup>P NMR spectra around 20 ppm. In addition, the CsF-digested <sup>1</sup>H NMR spectrum of 1 after activation shows a set of resonances in the aromatic region attributed to the decomposed species. Anal. Calcd for 1,  $\mathrm{Zr}_6$  $O_4OH_4(CH_3CO_2)_{2.8}(OH)_{0.4}(C_{33}H_{21}N_3O_8P_2RuCl_2(CO))_2$  $(C_{14}H_9O_6P)_{0.4}(MeOH)_{0.15}(DMF)_{0.5}$ : C, 35.88; H, 2.38; N, 3.35. Found: C, 36.09; H, 2.88; N, 3.23.

Synthesis of RuCl<sub>2</sub>(CO)<sub>3</sub>(THF). RuCl<sub>2</sub>(CO)<sub>3</sub>(THF) was prepared by modification of a procedure reported for the synthesis of [RuCl<sub>2</sub>(CO)<sub>2</sub>]"<sup>84</sup> A 200 mL Schlenk flask was charged with RuCl<sub>3</sub>·  $3H_2O$  (2 g, 0.76 mmol) and formic acid (67 mL). The flask was fitted with a reflux condenser and heated in an oil bath at 107  $^\circ C$  for 14 h under a nitrogen atmosphere. It is critical that the reaction be carried out at the specified temperature to obtain the desired product, as higher or lower temperatures lead to mixtures of unidentified products. After the mixture was cooled to room temperature, the excess formic acid was evaporated from the faint yellow solution under reduced pressure, and the resulting solid was washed with  $CH_2Cl_2$  (3 × 10 mL) to afford a white powder (1.75 g). The white solid was identified as the formic acid adduct RuCl<sub>2</sub>(CO)<sub>3</sub>(HCO<sub>2</sub>H) on the basis of the ATR-IR spectrum ( $\nu$ (CO) 2146 and 2066 cm<sup>-1</sup>,  $\nu$ (CO<sub>2</sub>) 1735 and 1141 cm<sup>-1</sup>  $\nu$ (OH) 3164 cm<sup>-1</sup>). Recrystallization from hot THF (5 mL) gave the THF adduct RuCl<sub>2</sub>(CO)<sub>3</sub>(THF) as a white low-density solid (1.5 g). ATR-IR:  $\nu$ (CO) 2137 and 2054 cm<sup>-1</sup>,  $\nu$ (THF) 1023 and 874 cm<sup>-1</sup>. ATR-IR spectra of these products are provided in Figure S21.

**Synthesis of** *cis*-[<sup>t</sup>**Bu**<sub>4</sub>**L**-**RuCl(CO)**<sub>2</sub>]**Cl.** A solution of RuCl<sub>2</sub>(CO)<sub>3</sub>(THF) (0.15 g, 0.46 mmol) in 1,4-dioxane (5 mL) was added to a solution of <sup>t</sup>Bu<sub>4</sub>(L) (0.41 g, 0.47 mmol) in 1,4-dioxane (5 mL) and stirred at 100 °C for 16 h. The reaction mixture was cooled to room temperature, and the solid was collected by filtration and washed with 1,4-dioxane (2 × 10 mL) and pentane (3 × 10 mL). The solid was dried in vacuo to afford a colorless powder (0.33 g, 65%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.52 (s, 36H, tBu), 6.90 (d, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 8.87 Hz, pyridine Ar-H), 7.86 (m, 5H, pyridine and benzoate Ar-H), 8.06 (m, 12H, benzoate Ar-H), 11.04 (s, 2H, NH). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  81.3 (s, 2P). ATR-IR:  $\nu$ (CO) 2062 and 2009 cm<sup>-1</sup>. Anal. Calcd for [<sup>t</sup>Bu<sub>4</sub>L-RuCl(CO)<sub>2</sub>]Cl, C<sub>51</sub>H<sub>57</sub>Cl<sub>2</sub>RuN<sub>3</sub>O<sub>10</sub>P<sub>2</sub>: C, 55.39; H, 5.20; N, 3.80. Found: C, 55.28; H, 5.17; N, 3.76.

Synthesis of cis-[H<sub>4</sub>L-RuCl(CO)<sub>2</sub>]TFA. A 20 mL scintillation vial was charged with [ ${}^{t}Bu_{4}L$ -RuCl(CO)<sub>2</sub>]Cl (0.25 g, 0.23 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), and CF<sub>3</sub>CO<sub>2</sub>H (1 mL). The vial was sealed, and the solution was stirred at room temperature for 16 h. Deionized water (5 mL) was added to the reaction mixture, resulting in formation of a white

precipitate. The product was collected by filtration, washed with deionized water (2 × 10 mL) and CHCl<sub>3</sub> (3 × 10 mL), and dried under reduced pressure to yield a white powder (0.21 g, 97%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  6.83 (d, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 8.25 Hz, pyridine Ar-H), 7.84 (m, 5H, pyridine and benzoate Ar-H), 7.99 (m, 4H, benzoate Ar-H), 8.09 (d, 4H, <sup>3</sup>*J*<sub>H-H</sub> = 8.00 Hz, benzoate Ar-H), 8.14 (d, 4H, <sup>3</sup>*J*<sub>H-H</sub> = 7.87, benzoate Ar-H), 10.72 (s, 2H, NH), 13.47 (br, 4H, CO<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  81.8 (s, 2P). <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  -74.0 (s, 3F). ATR-IR:  $\nu$ (CO) 2077 and 2022 cm<sup>-1</sup>. Anal. Calcd for [H<sub>4</sub>L-RuCl(CO)<sub>2</sub>]TFA-H<sub>2</sub>O, C<sub>37</sub>H<sub>27</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>13</sub>P<sub>2</sub>Ru: C, 45.48; H, 2.79; N, 4.30. Found: C, 45.28; H, 2.84; N, 4.32.

Synthesis of 2. A 20 mL scintillation vial was charged with ZrCl<sub>4</sub> (44 mg, 0.19 mmol), DMF (8 mL), and formic acid (3 mL). The mixture was sonicated for 20 min to afford a colorless solution. The solution was then added to a solution of [H<sub>4</sub>L-RuCl(CO)<sub>2</sub>]TFA (60 mg, 0.062 mmol) in DMF (4 mL) in a 20 mL scintillation vial. The vial was sealed with a Teflon-lined screw-top cap (Qorpak CAP-00554) and heated to 120 °C in a programmable oven for 18 h. After the mixture was cooled to room temperature, the solid was collected by centrifugation, washed with DMF ( $3 \times 10$  mL), and soaked in THF  $(4 \times 10 \text{ mL})$  for a total of 24 h. 2 was obtained as a nearly colorless microcrystalline powder (77 mg) after drying in vacuo. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CF<sub>3</sub>CO<sub>2</sub>H/DMSO- $d_6$ ):  $\delta$  82.4 (s, 2P). ATR-IR:  $\nu(CO)$  2067 and 2013 cm<sup>-1</sup>. On the basis of elemental analysis and NMR spectroscopic data obtained for 2 after THF solvent exchange and activation, the empirical formula is best given as  $Zr_6O_4(OH_4)(HCO_2)_4(L-RuCl(CO)_2)_2Cl_2(DMF)_2(H_2O)_2$  Anal. Calcd for 2,  $Zr_6O_4OH_4(HCO_2)_4(C_{33}H_{21}N_3O_8P_2RuCl(CO)_2)_2Cl_2$ -(H<sub>2</sub>O)<sub>2</sub>(DMF)<sub>2</sub>: C, 34.36; H, 2.45; N; 4.01. Found: C, 32.90; H, 2.85; N, 4.01.

Synthesis of cis-/trans-<sup>t</sup>Bu<sub>4</sub>L-RuCl<sub>2</sub>(CO). A solution of Me<sub>3</sub>NO in CH<sub>2</sub>Cl<sub>2</sub> (0.10 M, 3.8 mL, 0.38 mmol) was added to a solution of [<sup>t</sup>Bu<sub>4</sub>L-RuCl(CO)<sub>2</sub>]Cl (0.42 g, 0.38 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 20 mL scintillation vial, and the resulting mixture was stirred at room temperature for 1 h. The solution turned yellow immediately upon addition of Me<sub>3</sub>NO. The volatiles were removed under reduced pressure to yield a yellow powder (0.39 g, 96%). <sup>t</sup>Bu<sub>4</sub>L-RuCl<sub>2</sub>(CO) was obtained as a mixture of cis and trans isomers (cis:trans ratio  $\approx$ 1:2). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  1.51 (s, 36H, <sup>t</sup>Bu), 6.72 (d, 2H,  ${}^{3}J_{H-H}$  = 8.29 Hz, pyridine Ar-H, cis isomer), 6.75 (d, 2H,  ${}^{3}J_{H-H}$  = 8.10 Hz, pyridine Ar-H, trans isomer), 7.59 (t, 1H,  ${}^{3}J_{H-H} = 8.14$  Hz, pyridine Ar-H, cis isomer), 7.66 (t, 1H,  ${}^{3}J_{H-H} = 8.15$  Hz, pyridine Ar-H, trans isomer), 7.85 (dd, 8H,  ${}^{3}J_{H-H} = 11.79$  Hz,  ${}^{3}J_{P-H} = 6.30$  Hz, benzoate Ar-H, trans isomer), 7.93 (d, 8H,  ${}^{3}J_{H-H}$  = 8.73 Hz, benzoate Ar-H, trans isomer), 7.97 (br, 8H, benzoate Ar-H, cis isomer), 8.03-8.22 (8H, benzoate Ar-H, cis isomer), 10.14 (s, 2H, NH, trans isomer), 10.42 (s, 2H, NH, cis isomer).  $^{31}P\{^{1}H\}$  NMR (162 MHz, DMSO- $d_6$ ):  $\delta$  71.3 (s, 2P, cis isomer), 90.2 (s, 2P, trans isomer). ATR-IR:  $\nu$ (CO) 1964 cm<sup>-1</sup>.

Synthesis of cis-/trans-H<sub>4</sub>L-RuCl<sub>2</sub>(CO). A 20 mL scintillation vial was charged with <sup>t</sup>Bu<sub>4</sub>L-RuCl<sub>2</sub>(CO) (0.35 g, 0.32 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), CF<sub>3</sub>CO<sub>2</sub>H (1 mL), and concentrated HCl (0.1 mL). The vial was sealed and stirred at room temperature for 16 h. Et<sub>2</sub>O (10 mL) was added to the reaction solution, resulting in a white precipitate. The solid was collected by filtration, washed with  $Et_2O$  (3 × 10 mL), and dried in vacuo to afford the product as a light yellow powder (0.25 g, 91%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  6.65 (d, 2H,  ${}^{3}J_{H-H}$ = 8.02 Hz, pyridine Ar-H, cis isomer), 6.70 (d, 2H,  ${}^{3}J_{H-H}$  = 8.01 Hz, pyridine Ar-H, trans isomer), 7.59 (t, 1H,  ${}^{3}J_{H-H} = 7.84$  Hz, pyridine Ar-H, cis isomer), 7.66 (t, 1H,  ${}^{3}J_{H-H} = 8.19$  Hz, pyridine Ar-H, trans isomer), 7.83 (dd, 8H,  ${}^{3}J_{H-H} = 12.63$  Hz,  ${}^{3}J_{P-H} = 6.68$  Hz, benzoate Ar-H, trans isomer), 7.93 (dd, 4H,  ${}^{3}J_{H-H} = 13.56$  Hz,  ${}^{3}J_{P-H} = 6.67$  Hz, benzoate Ar-H, cis isomer), 7.98 (d, 8H,  ${}^{3}J_{H-H}$ = 8.23 Hz, benzoate Ar-H, trans), 8.03 (d, 4H,  ${}^{3}J_{H-H}$  = 8.01 Hz, benzoate Ar-H, cisisomer), 8.18 (dd, 4H,  ${}^{3}J_{H-H} = 12.51$  Hz,  ${}^{3}J_{P-H} = 6.93$  Hz, benzoate Ar-H, cis-isomer), 9.95 (s, 2H, NH, trans isomer), 10.17 (s, 2H, NH, cis isomer), 13.18 (br, 4H, CO<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DMSO- $d_6$ ):  $\delta$  71.5 (s, 2P, cis isomer), 90.3 (s, 2P, trans isomer). ATR-IR:  $\nu$ (CO) 1974 cm<sup>-1</sup>

Synthesis of 3. A 20 mL scintillation vial was charged with ZrCl<sub>4</sub> (49 mg, 0.21 mmol), DMF (8 mL), and glacial acetic acid (3 mL). The mixture was sonicated for 20 min to afford a colorless solution. The solution was then added to a solution of cis-/trans-H<sub>4</sub>L-RuCl<sub>2</sub>(CO) (60 mg, 0.070 mmol) in DMF (4 mL) in a 20 mL scintillation vial. The vial was sealed with a Teflon-lined screw-top cap (Qorpak CAP-00554) and heated to 120 °C in a programmable oven for 20 h. After the reaction mixture was cooled to room temperature, the solid was collected by centrifugation, washed with DMF  $(3 \times 10$ mL), and soaked in MeOH  $(4 \times 10 \text{ mL})$  for a total of 24 h. 3 was obtained as a colorless microcrystalline powder (61 mg) after drying in vacuo. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CF<sub>3</sub>CO<sub>2</sub>H/DMSO- $d_6$ ):  $\delta$  90.9 (s, 2P, trans isomer), 73.9 (s, 2p, cis isomer). ATR-IR:  $\nu$ (CO) 1988 cm<sup>-1</sup>. On the basis of elemental analysis and NMR spectroscopic data obtained for 3 after MeOH solvent exchange and activation, the empirical formula is best given as Zr<sub>6</sub>O<sub>4</sub>(OH<sub>4</sub>)(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>(L-RuCl<sub>2</sub>(CO))<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(MeOH) Anal. Calcd for 3; Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>- $(CH_{3}CO_{2})_{4}(C_{33}H_{21}N_{3}O_{8}P_{2}RuCl_{2}(CO))_{2}(H_{2}O)_{2}(MeOH)_{2}$ : C, 34.51; H, 2.60; N; 3.10. Found: C, 33.64; H, 2.87; N, 3.22.

**Synthesis of 2-a and 2-b.** A 20 mL scintillation was charged with 2 (0.154 g, 0.11 mmol of Ru), and a solution of KO'Bu in THF was added (0.1 M, 2.2 mL, 0.22 mmol). An immediate color change to yellow was observed upon KO'Bu addition, and the resulting mixture was gently stirred at room temperature for 16 h. The solid was collected via centrifugation and washed with THF ( $3 \times 10$  mL) to afford 2-a. 2-a was then treated with a solution of Me<sub>3</sub>NO in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M, 2.2 mL, 0.22 mmol) at room temperature for 16 h to generate 2-b. The solid was collected via centrifugation, washed with THF ( $4 \times 10$  mL), and dried in vacuo to afford a yellow microcrystalline powder (128 mg).

**General Procedure for Hydrosilylation Reactions.** In a N<sub>2</sub>filled glovebox, a 1 dram screw-top vial was charged with the catalyst (5 mol % based on Ru), 1,4-dioxane (1 mL), Et<sub>3</sub>SiH (0.4 mmol), substrate (0.2 mmol), and hexamethylbenzene as an internal standard (0.025 mmol). The vial was sealed with a Teflon-lined screw-top cap, and the reaction mixture was heated at 100 °C for 12 h. The products of the reaction were characterized by <sup>1</sup>H NMR and GC-MS/FID, and yields were determined by integration of <sup>1</sup>H NMR spectra with respect to the internal standard. For recycling experiments without regeneration, the catalyst was isolated from the reaction mixture via centrifugation, washed with 1,4-dioxane (3 × 2 mL), and resubjected to the catalytic conditions. Regeneration and recycling was carried out by washing the solid catalyst with 1,4-dioxane (3 × 2 mL) and then treating the solid with a solution of Me<sub>3</sub>NO in CH<sub>2</sub>Cl<sub>2</sub> as described above.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00482.

Spectroscopic (NMR, IR), GC-MS, XRPD, TGA, and  $N_2$  gas adsorption data, details of the Rietveld refinement of **2**, and additional data for catalytic hydrosilylation of benzaldehyde derivatives (PDF)

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#### Notes

The authors declare no competing financial interest.

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