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Reactivity of Silanes with (^{tBu}PONOP)Ruthenium Dichloride; Facile Synthesis of Chloro-Silyl Ruthenium Compounds and Subsequent Reactivity.

Nickolas H. Anderson,‡ James M. Boncella, Aaron M. Tondreau‡*

Abstract: The coordination of ^{tBu}PONOP (^{tBu}PONOP = 2,6-bis(di*tert*butylphosphinito)pyridine) to different ruthenium starting materials, to generate (^{tBu}PONOP)RuCl$_2$, was investigated. The resultant (^{tBu}PONOP)RuCl$_2$ reactivity with three different silanes was then investigated and contrasted dramatically with the reactivity of (^{iPr}PONOP)RuCl$_2$(DMSO) (^{iPr}PONOP = 2,6-bis(di*iso*propylphosphinito)pyridine) with the same silanes. The 16-electron species (^{tBu}PONOP)Ru(H)Cl was produced from the reaction of triethylsilane with (^{tBu}PONOP)RuCl$_2$. Reactions of (^{tBu}PONOP)RuCl$_2$ with both phenylsilane or diphenylsilane afforded the 16-electron hydrido-silyl species (^{tBu}PONOP)Ru(H)(PhSiCl$_2$) and (^{tBu}PONOP)Ru(H)(Ph$_2$SiCl), respectively. Reactions of all three of these complexes with silver triflate afforded the simple salt metathesis products of (^{tBu}PONOP)Ru(H)(OTf), (^{tBu}PONOP)Ru(H)(PhSiCl(OTf)), and (^{tBu}PONOP)Ru(H)(Ph$_2$Si(OTf)). Formic acid dehydrogenation was performed in the presence of triethylamine (TEA), and each species proved competent for gas pressure generation of CO_2 and H_2. The hydride species (^{tBu}PONOP)Ru(H)Cl, (^{tBu}PONOP)Ru(H)(OTf), and (^{tBu}PONOP)Ru(H)(PhSiCl$_2$) exhibited faster catalytic activity than the other compounds tested.

1. Introduction.

Organometallic pincer complexes have proven to be an important ligand class for transition metal catalysis. PONOP ligands, first reported by Goldberg and Brookhart,[1] have been used as supporting ligands on a number of transition metals, including early metals,[2] first-row metals,[3] and the noble metals of groups 9[4] and 10,[5] of which metal sigma complexes of methane have also been observed.[6] Importantly, even the larger tert-butyl substituted (^{tBu}PONOP) has demonstrated catalytic activity for hydrogenation,[3e, 7] hydrosilylation,[3i] and olefin-isomerization reactions.[2]

PV-work performed *via* gas generation spurs our current investigations into organometallic catalyzed formic acid (FA) dehydrogenation. Although many systems focus on the potential for hydrogen storage,[8] the ability of gas pressure to perform work, like spinning an actuator, could obviate the need for steel gas cylinders if sufficient pressure can be generated in a short period of time. Ruthenium mediated decomposition of FA into H_2 and CO_2 is some of the oldest work published in the field,[9] yet pressure generation is rarely discussed.[10] Most of these Ru systems have drawbacks, such as the requirement for dilute FA concentrations. A recent report by Huang using mono-deprotonated (^{tBu}PN^{H}NNP)RuH(CO) exhibiting robust performance as a formic acid dehydrogenation catalyst, yet requires slow addition of formic acid.[11] Iridium has proved competent under high molarity conditions of FA:[21] a report by Li on iridium(III) catalysts that was robust in 5M concentrations of FA under aqueous conditions.[12] Williams was able to perform catalysis with an Ir(I) system and base in neat FA with turnover frequencies of over 3000 hr^{-1}.[13]

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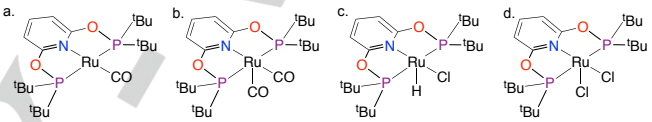

Figure 1. The coordinatively unsaturated compounds: a) (^{tBu}PONOP)Ru(CO), b) (^{tBu}PONOP)Ru(CO)$_2$, c) (^{tBu}PONOP)Ru(H)Cl, and d) (^{tBu}PONOP)RuCl$_2$ (**1**) reported by Milstein.

For the potential PONOP ligands have for transition metal chemistry, a dearth of reported ruthenium complexes supported by PONOP chelates persists in the literature. Milstein's initial report of ^{iPr}PONOP and ^{tBu}PONOP ruthenium complexes in 2009,[14] albeit extensive, is the only synthetic reference for this class of compounds. More recent DFT work has been performed on exploring carboxylation of arenes,[15] as well as a report of immobilizing several of Milstein's complexes, among other PONOP supported metal complexes, on silica-polyamine composite surfaces.[16] The majority of known ^{tBu}PONOP-supported ruthenium complexes that have been reported are 18-electron, coordinatively saturated complexes bearing a CO ligand in the plane of the chelate. Exceptions to this are synthesis of (^{tBu}PONOP)RuCl$_2$ (**1**) and (^{tBu}PONOP)RuHCl (**2**), reported on milligram scales and requiring the removal of free PPh$_3$. Two CO complexes, (^{tBu}PONOP)Ru(CO)$_2$ and (^{tBu}PONOP)Ru(CO) (Figure 1), are also reported. This work offers an alternative synthesis of **1** that was performed on the gram scale, and subsequently seeks to expand the number of fundamental transformations known for **1**. This work provides entry into 16-electron, coordinatively unsaturated ruthenium complexes derived from **1**. Complex **2** piqued our interest to investigate *tert*-butyl PONOP derivatives for FA dehydrogenation. This suite of complexes is then shown to be competent for FA dehydrogenation under basic conditions.

2. Results and Discussion

2.1 Synthesis of PONOP-supported ruthenium hydride complexes.

Initial work on ^{tBu}PONOP/ruthenium systems focused on synthesizing **1** on larger scales in order to more fully explore its chemistry. The previous method of synthesis used the

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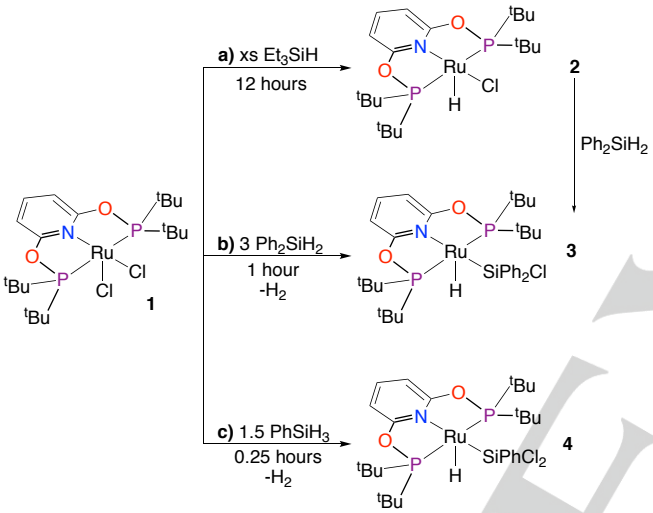
ubiquitous $(PPh_3)_3RuCl_2$ as the ruthenium source, and for larger-scale synthesis we felt the PPh_3 removal, although readily achieved *via* column chromatography, should be circumvented in the interest of atom economy. We first turned to $(dmso)_4RuCl_2$, (dmso = dimethylsulfoxide) a source of ruthenium that previously proved extremely versatile in our hands. Initial results, upon reflux in 1,2-dichloroethane (DCE), appeared favorable, as the yellow solution darkened to green-blue over the course of hours. Upon cooling, however, the solution lost its green color and ruthenium complex appeared to coordinate a dmso molecule and form the six-coordinate complex (^{tBu}PONOP)$RuCl_2$(dmso). We felt the synthesis could be improved by using a different ruthenium source, and $[(cymene)RuCl_2]_2$ was used and proved to be the most facile way of generating the desired complex **1**. Refluxing ^{tBu}PONOP with half an equivalent of $[(cymene)RuCl_2]_2$ in DCE overnight gave **1** in good yields (>70 %) consistently in gram-scale quantities. With **1** in hand, we proceeded to investigate its reactivity.



Scheme 1. Reactivity of **1** with Si-H complexes and the formation of **2**, **3**, and **4**.

Historic use of silyl-hydrides to form ruthenium hydride bonds from ruthenium chloride bonds has proven successful;[17] we opted for the use of silanes rather than more aggressive metal-hydride reagents. Et_3SiH was added to **1** in a ten-fold excess, and after stirring in THF with heating for one hour, the solution's green color had turned red. The ^{31}P NMR spectrum of an aliquot of the reaction mixture revealed >90 % conversion to the desired (^{tBu}PONOP)Ru(H)Cl (**2**) (Scheme 1a). Allowing the reaction to stir for two more hours gave complete conversion to **2**. Regardless of the quantity of Et_3SiH used, heating, or length of time, **2** remained the only product from the reaction. In this fashion we were able to generate **2** on a half-gram scale in good yields (>90 %). Single crystal X-ray diffraction studies of **1** and **2** were performed and the details of these structures are reported in the SI (Figure S13 and S14).

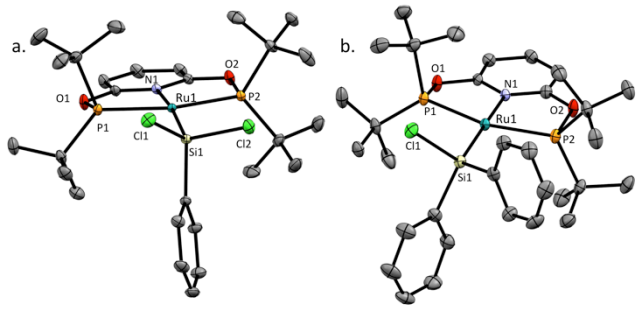


Figure 2. Molecular Structure of **3** and **4** with ellipsoids displayed at 50% probability. Hydrogen atoms and outer sphere solvents have been removed for clarity.

The reaction of **1** with Ph_2SiH_2 was performed similarly to that of Et_3SiH; initially two equivalents of Ph_2SiH_2 were added to a solution of **1** in THF. Upon addition, the solution turned a red color concurrent with gas evolution. An aliquot of the solution analyzed by ^{1}H and ^{31}P NMR spectroscopy revealed the presence of two-differing Ru-H species: roughly 10 % of the material was consistent with **2**, and the remaining material contained resonances suggesting a diphenylsilyl bound moiety. An orange powder was isolated after work-up and identified as (^{tBu}PONOP)Ru(H)$(Si(Ph)_2Cl)$ (**3**). The yield of **3** could be increased with the use of 2.5 equivalents of Ph_2SiH_2, followed by removal of THF and stirring the material in *n*-hexane for at least one hour at room temperature prior to cooling and isolation (Scheme 1b). Isolated **2** and one equivalent of Ph_2SiH_2 were combined in a sealed NMR tube. An unidentified intermediate was observed, but upon crystallization, **3** formed. This suggests that **2** is an intermediate in the formation of **3**, albeit with a second intermediate formed from **2** and Ph_2SiH_2.

Addition of 1.5 equivalents of $PhSiH_3$ to **1** resulted in the immediate color change from green to red with concurrent effervescence of the solution. An orange powder was isolated after work-up that was identified as (^{tBu}PONOP)Ru(H)$(SiPh(Cl)_2)$ (**4**, Scheme 1c). The ^{31}P NMR spectra of complexes **3** and **4** each contained resonances at 233.47 ppm and 231.15 ppm, respectively. These shifts are downfield of complexes **1** and **2** with shifts of 182.90 ppm and 212.13 ppm, respectively. The Ru-H resonances in the ^{1}H NMR spectra are found as triplets upfield at -30.24 ppm and -30.59 ppm, with chemical shifts that are similar to the chemical shift of **2** (-31.13 ppm). Solid-state structures of **3** and **4** are provided in Figure 2.

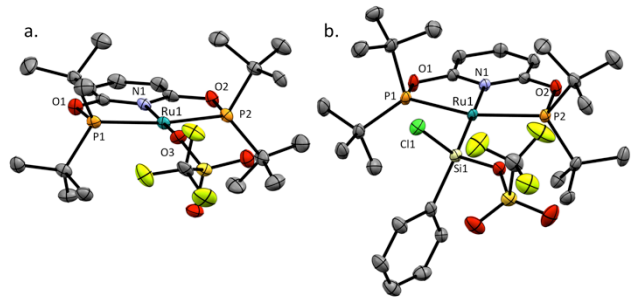


Figure 3. Molecular Structures of **2-OTf** (a.) and **4-OTf** (b.).

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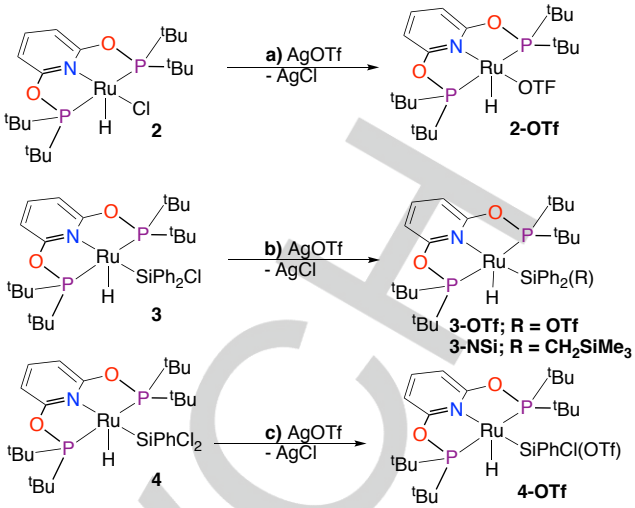
Substitution of the chlorine atoms was achieved *via* addition of one equivalent of [Ag][OTf] to a fluorobenzene solution of **2** and trifluoromethanesulfonate (triflate, OTf) was installed. The reaction produced a flocculent white precipitate of AgCl, concurrent with a deepening of the red color of the reaction solution. Spectroscopic analysis of the isolated orange/red material is consistent with (^{tBu}PONOP)Ru(H)(OTf), **2-OTf**. The reaction of **3** and **4** performed in a similar fashion resulted in the formation of the OTf complexes, (^{tBu}PONOP)Ru(H)(SiPh$_2$(OTf)) and (^{tBu}PONOP)Ru(H)(SiPh(OTf)(Cl)), **3-OTf** and **4-OTf**, respectively (Scheme 2). The ^{1}H NMR spectra of **2-OTf**, **3-OTf**, and **4-OTf** revealed Ru-H resonances that are shifted slightly from the chloride congeners. -31.32, -29.95, and -30.26 ppm, respectively. Solid-state structures of **2-OTf** (Figure 3(a)) and **4-OTf** (Figure 3(b)) were obtained and revealed a coordinating OTf moiety. Complex **3** was alkylated using NaCH$_2$SiMe$_3$ to support the generality of nucleophilic substitution at silicon (**Scheme 2c**) to yield (^{tBu}PONOP)Ru(H)(SiPh(CH$_2$SiMe$_3$)(Cl)) **3-NSi**. With a Ru-H resonance at -30.57 ppm in the ^{1}H NMR spectrum and a ^{31}P NMR resonance at 228.6 ppm, the spectroscopic profile was similar to the other silyl complexes examined. The solid-state structure was obtained and confirmed the identity of **3-NSi** (SI Figure S15).

2.2 Catalytic dehydrogenation of formic acid with (^{tBu}PONOP)ruthenium complexes

Initial formic acid (FA) dehydrogenation catalysis was investigated using complexes **1**, **2**, **1-OTf$_2$**, and **2-OTf** (Table 1). As benchmarks for comparison, the time for which the catalyst takes to reach 50 and 150 psig is reported. Our investigation began with **1** in 4 mL chlorobenzene (0.1 mol%) with 1 mL of FA injected into a 70 mL stainless steel pressure reactor heated to 80 ºC and resulted in little generation of gas pressure. Common with other Ru based FA decomposition catalysts, this system required the addition of base to proceed.[18] The use of the FA/triethyl amine (TEA) azeotrope (5:2 ratio) was investigated next. The volume was held constant using 1.5 mL of the azeotrope and the volume of chlorobenzene was adjusted to total 4mL. Addition of the azeotrope to the catalyst solution resulted in a rapid generation of gas pressure, reaching 150 psig within 270 seconds. For consistency, we premade a catalyst solution containing TEA and chlorobenzene, to which FA was added. In order to maintain a constant volume for the reaction, a 1:1 v/v solution of chlorobenzene (2 mL) and TEA (2 mL) was made and the reaction was performed again (Table 1, entry 3). This resulted in an increase in the rate of generation of gas pressure, with internal cell pressures reaching 150 psig in just over 120 seconds. The decomposition of FA using **2, 2-OTf** and **3** was investigated under the same conditions as **1**. These complexes show an increase in FA decomposition activity (Table 1, entry 4, 5, and 6). Their reactivity can also be compared to that of *in situ* generated (^{tBu}PONOP)Ru(OTf)$_2$ (**1-OTf$_2$**). **1-OTf$_2$** was synthesized *via* addition of two equivalents of AgOTf to a stirring catalyst solution of **1**. All complexes tested show remarkable FA decomposition activity under these conditions with initial turnover frequencies (TOF) ranging from 1.9 - 3.7 x 10^4 hr^{-1} (Table 1).



Scheme 2. Reactivity of **1** with Si-H complexes

Hydride complexes **2**, **3**, and **2-OTf** showed the fastest rates of FA decomposition. **2** and **2-OTf** showed nearly identical turnover frequencies and times to reach benchmark pressures. The decrease in reactivity seen with **3** can be attributed to the increase in size/decrease in availability to the metal center due to the steric effects of the bound silyl ligand. Further reactivity was studied with complex **2**. Lower catalyst loadings of **2** (0.50 and 0.01 mol%, Table 1, entry 14-16 gave interesting results. At 0.50 mol% catalyst loading, **2** gives a nearly identical gas generation profile as when performed with 0.10 mol% loading. When lowered to 0.01 mol% percent, the reaction stalls at a pressure far below that of the calculated equilibrium pressure, likely a result of catalyst decomposition. Alterations in temperature also have quite a large effect on the overall rate and final equilibrium pressure. Performing this reaction with **2** at ambient temperatures results in a decrease in the rate of the reaction, taking nearly 20 minutes to produce 50 psig of pressure and nearly 6 hours to reach equilibrium (~190 psig). Increasing the temperature to 40 ºC increased the initial TOF of the reaction by over an order of magnitude. Turnover number of 190,000 was obtained from slow addition of FA to **2** under slightly different conditions (See SI). It was noted that if exposed to oxygen prior to catalysis, all catalyst complexes suffered from decomposition leading to low catalytic activity.

The effect of base (TEA) concentration on the rate of FA decomposition was also tested. To maintain a consistent total volume, the volume of the reaction mixture was adjusted with chlorobenzene. Base has a profound effect on the rate and total pressure of the catalysis (Table 1, entry 11-13). At lowered concentrations of added base (1mL TEA) the rate of FA decomposition proceeds at a much slower initial rate, with an initial TOF of only 1383 hr^{-1}. This low TOF is not constant, and as more of the FA is consumed, the rate exponentially increases (Supplementary Figure 11). The addition of even more TEA to the solution (3 mL TEA) shows nearly an identical initial TOF (TOF = 33500 hr^{-1}) as compared to that of the standard (TOF = 36700 hr^{-1}). However, as the reaction proceeds, the rate of reaction begins to slow as the concentration of FA decreases. This would suggest that there is an optimal concentration of both HCO$_2$H and [HCO$_2$][HNEt$_3$] in solution that provides peak rates of decomposition. The three different reaction mixtures showed increasingly lower equilibrium pressures with increased amount

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of base used. This is attributed to the amount of $[HCO_2]^-[HNEt_3]^+$ present in solution which alters the effective FA concentration and thus the overall equilibrium pressure. When comparing the gas generation profiles for added base at 50 mol% versus the premade azeotrope at 28 mol%, we see a drastic decrease in activity of the former (Table 1, entry 11). In either case, this system exhibits a high activity for FA dehydrogenation, with the ability to generate high *pressure* in a relatively short timeframe. Our results demonstrate that this seemingly simple reaction demonstrates a remarkable complexity that we continue to explore and will report on in due course.

Table 1.

Entry	Comp.	mol $\%_{cat.}$	Temp.	mol $\%_{TEA}$	50 psig (sec)	150 psig (sec)	Equil. (sec)	TOF hr^{-1} c.
1	**1**	0.10	80	0.0	-	-	-	-
2	**1**	0.10	80	28.6[a]	124	271	414	6000
3	**1**	0.10	80	100	36	136	360	21000
4	**2**	0.10	80	100	21	69	282	36000
5	**3**	0.10	80	100	24	84	303	32000
6	**1-OTf$_2$**	0.10	80	100	40	135	441	19000
7	**2-OTf**	0.10	80	100	23	73	282	33000
8	**2**	0.10	80	100	21	69	282	36000
9	**2**	0.10	40	100	90	417	1248	8000
10	**2**	0.10	23	100	1128	~17200	~6 hr.	600
11[b]	**2**	0.10	80	50	558	846	1080	1000
12	**2**	0.10	80	100	21	69	282	36000
13[b]	**2**	0.10	80	150	23	144	415	33000
14[d]	**2**	0.50	80	100	20	80	280	7000
15	**2**	0.10	80	100	21	69	282	36000
16	**2**	0.01	80	100	140	--	--	5000

[a] 1.58 mL of the FA/TEA azeatrope was used and the volume of the C_6H_5Cl was adjusted. [b]Volume of TEA was altered and the volume of the C_6H_5Cl was adjusted. [c.] Initial TOF calculated based off 20% conversion of FA to CO_2 and H_2 , TOF have been rounded down. [d]Much of 2 was still suspended in the solution in particulate form at such high concentrations, suggesting a lower catalyst concentration than intended.

2. Summary and Conclusions

A route to gram-scale isolation of (^{tBu}PONOP)$RuCl_2$ (**1**) was described along with the conversion of **1** into several hydride containing species. The synthesis of **2** differs from the previous report by using Et_3SiH with **1** rather than chelating ^{tBu}PONOP to $(PPh_3)_3RuHCl$. Similar Ru-H formation was observed with $PhSiH_3$ and Ph_2SiH_2. These reactions also formed Ru-Si bonds, Si-Cl bonds, and released H_2, an interesting sequence of bond making/breaking that occurs in the same pot. This sparingly studied class of molecules is primed for further development and related reactivity will be reported in due course.

The Ru-H complexes formed in this study prove efficient as catalysts for decomposition of FA and show rapid pressure generation in concentrated FA solutions. Base is required for catalysis, and different formulations of reactants alter the velocity and overall pressure generation. The TOF's observed are among the highest observed for ruthenium calalysts and the catalysts are also robust being stable for upwards of 190,000 turnovers.

Experimental Section

All air- and moisture-sensitive manipulations were carried out using standard Schlenk techniques or in an MBraun dry box containing a purified nitrogen atmosphere. THF, diethyl ether, toluene, and n-hexane were dried on molecular sieves and shaved sodium before use. Chlorobenzene was purchased from Sigma Aldrich and filtered over dry, neutral alumina and stored over 4 Å molecular sieves. Triethylamine was purchased from Sigma Aldrich and dried over K_2CO_3 and distilled under reduced pressure before use. THF-d_8, and C_6D_6 were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. The chemicals: $((cymene)RuCl_2)_2$, AgOTf, $PhSiH_3$, Ph_2SiH_2, Et_3SiH, were purchased from Fisher Scientific and were used after degassing. The compounds: ^{tBu}PONOP,[14] ^{iPr}PONOP,[14] $RuCl_2(dmso)_4$,[19] and (trimethylsilyl)methyl sodium[20] were synthesized according to published procedures. Crystallographic data for all structures is available from the Cambridge Structural Database with the following CCDC codes; **1:** 1548404, **2:** 1548405, **3:** 1548406, **4:** 1548407, **2-OTf:** 1548408, **4-OTf:** 1548409, and **3-NSi:** 1548410.

Alternative Synthesis of (^{tBu}PONOP)Ru(H)(Cl) (2).

In an inert atmosphere drybox, 0.500 g (0.875 mmol) of **1** was added to a 20 mL scintillation vial and dissolved in 5 mL of THF. Triethylsilane (0.250 g, 2.15 mmol, 2.5 equivalents) was added at once and the reaction was stirred for 12 hours at 30 °C The solution turned from green to deep red. Volatiles were removed and the residue was mobilized with n-hexane (~ 5 mL), and the slurry cooled to -30 °C, at which time the red solid was collected on a glass frit and held under reduced pressure to a constant mass to yield 0.340 g (72 %) of (^{tBu}PONOP)Ru(H)(Cl) (**2**). A second crop of material could be collected by concentrating the mother liquor, cooling to -30 °C, and collecting the solid to bring the total yield to 0.420 g (89 %). Spectroscopic analysis gave identical results to a previously prepared sample. Single crystals were grown from slow evaporation of an n-hexane solution of **2**.

Synthesis of (^{tBu}PONOP)Ru(H)(Si(Ph)$_2$Cl) (3).

In an inert atmosphere drybox, 0.500 g (0.875 mmol) of **1** was added to a 20 mL scintillation vial and dissolved in 5 mL of THF. Diphenylsilane (0.484 g, 2.625 mmol, 3 equivalents) was added dropwise. Upon addition, the solution turned from green to deep red with concomitant effervescence, presumably H_2 release. The solution was allowed to stir for one hour, at which time volatiles were removed and the residue was mobilized with n-hexane (~ 5 mL), generating an orange solid. The slurry was stirred at room temperature for one hour as increasing amounts of orange solid formed. The reaction was cooled to -30 °C and the orange solid collected on a glass frit and held under reduced pressure to a constant mass to yield 0.380 g (63 %) of (^{tBu}PONOP)Ru(H)(Si(Ph)$_2$Cl) (**3**). A second crop of material could be collected by concentrating the mother liquor, cooling to -30 °C, and collecting the solid to bring the total yield to 0.480 g (76 %). Single crystals were grown by a slow diffusion of n-hexane into a fluorobenzene solution of **3**.^{1}H NMR (300 MHz, C_6D_6, 25 ºC, TMS) δ = 8.20 (4H, d, J=7 Hz), 7.59 (1H, s), 7.28 (4H, m), 7.12 (2H, s), 6.78 (1H, t, J=7Hz), 6.21 (2H, d, J=7 Hz),

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1.16 (18H, s), 1.02 (18H, s), -30.25 (1H, t, J=20 Hz); ^{13}C NMR (300 MHz, C_6D_6, 25 ºC, TMS) δ = 163.6, 151.9, 138.6, 136.4, 126.9, 126.6, 99.9, 43.2, 39.2, 27.2; ^{31}P NMR (300 MHz, C_6D_6, 25 ºC, TMS) δ = 230.4; Analysis (calcd., found for $C_{27}H_{45}Cl_2NO_2P_2RuSi$): C (47.86, 46.88), H (6.69, 6.63), N (2.07, 1.83).

Synthesis of (^{tBu}PONOP)Ru(H)(SiPh(Cl)$_2$) (4).

In an inert atmosphere drybox, 0.500 g (0.875 mmol) of **1** was added to a 20 mL scintillation vial and dissolved in 5 mL of THF. Phenylsilane (0.142 g, 1.312 mmol, 1.5 equivalents) was added dropwise. Upon addition, the solution turned from green to deep red with concomitant effervescence, presumably H_2 release. The solution was allowed to stir for one hour, at which time volatiles were removed and the residue was mobilized with n-hexane (~ 5 mL), generating an orange solid, and the slurry cooled to -30 °C, after which time the orange solid was collected on a glass frit and held under reduced pressure to a constant mass to yield 0.430 g (79 %) of (^{tBu}PONOP)Ru(H)(Si(Ph)(Cl)$_2$) (**4**). A second crop of material could be collected by concentrating the mother liquor, cooling to -30 °C, and collecting the solid to bring the total yield to 0.510 g (93 %). Single crystals were grown from a slow diffusion of n-hexane into a fluorobenzene solution of **4**. ^{1}H NMR (300 MHz, C_6D_6, 25 ºC, TMS) δ = 8.44 (2H, d, J=7 Hz), 7.38 (1H, s), 7.32 (2H, m), 7.04 (1H, s), 6.76 (1H, t, J=7Hz), 6.16 (2H, d, J=7 Hz), 1.21 (36H, s), -30.16 (1H, t, J=20 Hz); ^{13}C NMR (300 MHz, C_6D_6, 25 ºC, TMS) δ = 163.51, 151.51, 139.63, 133.60, 127.07, 100.20, 43.36, 39.33, 27.71, 27.47; ^{31}P NMR (300 MHz, C_6D_6, 25 ºC, TMS) δ = 229.4; Analysis (calcd., found for $C_{33}H_{50}ClNO_2P_2RuSi$): C (55.10, 51.26), H (7.97, 6.54), N (1.95, 1.83).

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Author Contributions

‡ Authors contributed equally to this manuscript.

Keywords: Ruthenium • Catalysis • Silyl • dehydrogenation • Formic Acid • PONOP

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