A Commercially Available Ruthenium Compound for Catalytic Hydrophosphination

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Abstract

Hydrophosphination with a commercially available ruthenium compound, bis(cyclopentadienylruthenium dicarbonyl) dimer ($[\text{CpRu}(\text{CO})_2]_2$), was explored. Styrene derivatives or Michael acceptors react readily with either primary or secondary phosphines in the presence of 0.1 mol % of $[\text{CpRu}(\text{CO})_2]_2$ under photolysis with an inexpensive and commercially available UV-A 9W lamp. In comparison to related photoactivated hydrophosphination reactions with $[\text{CpFe}(\text{CO})_2]_2$ as a catalyst, these ruthenium-catalyzed reactions proceed at greater relative rates with lower catalyst loadings.

¹ Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ijch.2010xxxxx>.

Introduction

Selective P–C bond formation continues to be a synthetic challenge despite the myriad of applications phosphines have in synthetic and catalytic chemistry.^[1] Metal-catalyzed hydrophosphination is at the fore of P–C bond formation because it proceeds with 100% atom economy with the potential for high selectivity, producing regio-, chemo-, and enantiospecific products.^[2] The transformation appears to be on the rise in global interest and mechanistic understanding continues to increase.^[1h]

However, hydrophosphination catalysis has its challenges.^[2b] Precious metal catalyzed reactions remain among the most popular and lead the field in selectivity.^[2a, 2b, 3] Many d⁰ metal catalysts exhibit great activity and substrate scope but still have substantial limits. Recent noteworthy successes including high enantioselectivity and the synthesis of other value-added molecules such as chelating ligands and phosphorus heterocycles demonstrate that continued study of this transformation will be highly fruitful.^[3j, 4]

Exploration of ruthenium-based hydrophosphination reactivity has been productive and intriguing. In a report by Dixneuf, simple ruthenium complexes, including Cp*Ru(COD)Cl and Cp*Ru(PPh₃)₂Cl, were used generate vinyl phosphines from propargyl alcohols. However, reaction conditions were somewhat harsh at >100 °C for 24 hours, with catalytic base, and relatively high catalyst loadings.^[5] Rosenberg and coworkers have garnered tremendous mechanistic understanding through investigation of stoichiometric P–C bond formation with ruthenium.^[1h, 6] At the core of that work is a concerted, inner-sphere P–C bond forming event,

most likely an insertion reaction, as well as an understanding of product liberation from the metal through a fully developed stoichiometric cycle akin to a catalytic process.

Substantial advances in iron-catalyzed hydrophosphination have been made in recent years. The field has been led by the groups of Gaumont using iron salts for the selective hydrophosphination of alkenyl arenes, Nakazawa for iron promoted hydrophosphination of internal alkenes with diphenyl phosphine, and Webster for iron catalyzed hydrophosphination of alkenes and alkynes with both primary and secondary phosphines.^[4e, 7] We have reported photoactivated hydrophosphination catalysis with $[\text{CpFe}(\text{CO})_2]_2$ (**1**), including rapid double hydrophosphination of terminal alkynes to form 1,2-diphosphinoethane products.^[3e, 3i] This study targeted the potential hydrophosphination reactivity of $[\text{CpRu}(\text{CO})_2]_2$ under photoactivation with a key question: Would the reactivity and activity of ruthenium be substantially different than iron? This question informs a broader hypothesis that limitations in iron-catalyzed hydrophosphination can be overcome with greater understanding, even of its congener. Addressing this hypothesis would both advance hydrophosphination in general as well as aid in expanding this reaction in a more sustainable way.

More than merely a comparison of congeners, the similarity of activation via photo-induced splitting of the dimers into 17-electron intermediates is critical to this comparison. Whereas **1** is activated into two equivalents of the 17-electron compound $\text{Cp}(\text{CO})_2\text{Fe}\cdot$ by visible light, the ruthenium compound **2** is activated by near UV light (~ 330 nm) to also yield two $\text{Cp}(\text{CO})_2\text{Ru}\cdot$ (eq 2).^[8] The related photoactivation is a key piece of the comparative study of these compounds.

Results and discussion

Hydrophosphination of activated alkenes with phenylphosphine was initially explored. Treatment of a three-to-one mixture of phenylphosphine and alkene with 0.1 mol % of **2** in benzene-*d*₆ at ambient temperature under irradiation by a broad wavelength 9-W UV/A lamp (See SI for spectrum) resulted in hydrophosphination of the alkene in conversions greater than 90% as determined by ¹H and ³¹P NMR spectroscopy (Table 1). Three equivalents of phosphine were generally optimal because lower phosphine loadings increased formation of tertiary phosphine products via double P-H activation, while higher loadings did not provide improved selectivity. Some initial screening reactions were conducted at 1.0 mol % catalyst loading, but it was found that 0.1 mol % of **2** achieved high conversions for all substrates tested in two hours or less of reaction time. Thus, activity was not adversely affected by the decreased catalyst loading. Reactions were irradiated using a commercial UV/A lamp (λ = 360 nm) and shielded from ambient light. The UV/A lamp does produce excess heat and shielded reactions were measured at temperatures of 25–30 °C, depending on the total reaction time and if the photoreaction chamber had recently been in use or completely cooled. Precise measures to control reaction temperatures within the range of 25–30 °C were not undertaken.

Table 1 Hydrophosphination of styrene substrates and Michael acceptors

Substrate	Time ^[a]	Major product	Minor product	Conversion ^[b]
60			100 (95 : 5)

40			100 (95 : 5)
60			100 (95 : 5)
70			100 (95 : 5)
60			100 (99.6 : 0.4)
120			95 (96 : 4)
12			100 (93 : 7)
18 h			100 ^{[c][d]} (81 : 19)

Products were unambiguously identified by comparing ^1H and ^{31}P spectra to literature values. Products were not isolated and conversions were determined by integration of ^{31}P NMR spectra and confirmed by integration of ^1H NMR when peaks were not obscured by overlapping with starting material or other products. If there is not significant noise in the baseline, ^{31}P NMR is generally accurate for integration of products, though not as accurate as ^1H NMR. As a result, some ratios may be slightly less accurate than if ^1H NMR integration could be employed. Consumption of unsaturated substrate was determined by ^1H NMR spectroscopy. [a] Time in minutes unless specified. [b] values in parenthesis are ratio of major to minor products. [c] catalyst loading = 1 mol %. [d] Reaction run at a ratio of 1 : 1 alkene to phosphine.

Increased, and different, activity was observed with **2** as compared to **1**. A difference in reactivity was observed for electron rich and poor styrene substrates with **1**, with electron-poor styrene substrates being more readily converted.^[3e] This trend was not observed with **2**. For some substrates, the opposite trend was observed with more electron-rich styrene substrates reacting with a greater relative rate. Steric bulk also appears to increase reactivity. However, a clear and conclusive pattern is difficult to discern due to the fast and similar reaction times of styrene and styrene derivatives. First, and unlike **1**, styrene was a viable substrate, with complete consumption in 60 minutes. Electron donating para-alkyl substituted styrene derivatives, ^tBu and Me, were both completely consumed in less than one hour under irradiation at ambient temperature. Complete consumption of the bulkier *p*-tert-butylstyrene occurred faster than *p*-methylstyrene. Electron-poor styrene derivatives required similar, in the case of the bulkier *p*-trifluoromethylstyrene, or longer reaction times in the case of *p*-bromostyrene to be fully consumed with each undergoing reaction times of 60 and 70 minutes, respectively, for completion.

Michael acceptors were excellent substrates for this reaction, as anticipated. When using methyl acrylate as the unsaturated substrate, complete consumption of methyl acrylate was observed in less than 12 minutes, and produced the secondary and tertiary hydrophosphination products in 93% and 7% yields, respectively.^[2b, 3g, 7b, 9] In control reactions run under irradiation in the absence of **2**, complete consumption of acrylate substrate was observed after 4 hours (95 : 5). The UV initiated hydrophosphination of Michael acceptors is well established.^[10]

The identity of the phosphine is important. Reaction of phenylphosphine (3 eq) and 2,3-dimethyl,1-3-butadiene with 1 mol % of **2** under irradiation afforded the 1,4-addition product in 91% conversion at 2 hours reaction time as determined by NMR spectroscopy (Table 2). In contrast, the reaction of cyclohexylphosphine (3 eq) and 2,3-dimethyl,1-3-butadiene with 1 mol %

of **2** under irradiation allowed for observation of the 1,4-addition product in 9% conversion at 2 hours and 12% at 18 hours of reaction time. Steric factors may be at work, but the substantial difference in activity suggests that electronic factors cannot be ignored.

The reversed behavior of electron donating and withdrawing substituents is not the most important distinction between the iron and ruthenium compounds as hydrophosphination catalysts. Treatment of a 1 : 1 mixture of diphenylphosphine and styrene with 1 mol % of **2** for nearly one day under irradiation resulted in the 97% conversion to the expected hydrophosphination as determined by ^{31}P NMR. Reducing the catalyst loading to 0.1 mol % of **2** resulted in 84% conversion to the hydrophosphination product after 24 hours and a 92% conversion after 48 hours. While iron compound **1** had a particularly low conversion with styrene (NB: there appeared to be some competitive radical chemistry for this substrate), para-substituted derivatives were effective substrates.^[3e] However, even for the most active styrene derivatives, iron exhibits more modest activity than ruthenium does. Thus, it is reasonable to conclude that **2** is a more active catalyst for hydrophosphination catalysis than is **1**. This increase in activity is offset by the substantial difference in cost for these two catalysts. A recent search of the Sigma-Aldrich web catalog revealed pricing for **1** of approximately 0.38 USD per gram and 361 USD per gram for **2**. From an economic standpoint, it seems more likely that the activity of iron can be increased to match that of ruthenium rather than the loading reduced to justify its cost. That course analysis supports a sustainability argument for the continued study of iron catalysts for this reaction.

The comparative study for **1** and **2** is limited to diphenylphosphine because compound **1** is so poorly effective in hydrophosphination with primary phosphine substrates. Indeed, our main objective in investigating ruthenium was the potential for observing α -phosphinidene elimination with a heavier metal that may promote singlet-like phosphinidene chemistry rather than the triplet-

like phosphinidene transfer promoted by **1**.^[11] The absence of phosphinidene transfer with **2** and the observation of hydrophosphination instead is consistent with our developing hypothesis that greater reactivity with unsaturated substrates diminishes transfer of low-valent fragments.^[12] In any case, comparison of the same phosphine and unsaturated substrates for both catalysts is important for benchmarking hydrophosphination catalysis.^[9b]

Other substrates, however, were not amenable to hydrophosphination using **2**. Reaction of 1-hexene with phenylphosphine and 1 mol % of **2** under irradiation resulted in only 4% consumption of 1-hexene to the secondary phosphine product. Similar results were obtained in reactions with ethyl vinyl ether and cyclohexene (Table 2). Unactivated alkenes are challenging substrates for any heterofunctionalization reactions, and only one catalyst is effective in the hydrophosphination of these substrates.^[3j] ^[9b] Alkynes are more amenable than unactivated alkenes, but these are still poor substrates by any reasonable measure. Reaction of phenylacetylene and phenylphosphine with 1 mol % of **2** under irradiation resulted in 46% consumption of phosphine by ³¹P NMR spectroscopy (Table 2). However, the products were largely unidentified and primarily not the expected vinylphosphine product or possible 1,2-bis(phenylphosphino)-1-phenylethane, which is the anticipated product of iron catalyst **1** or Cp(CO)₂FeMe by Nakazawa in a double hydrophosphination reaction.^[3i, 13] Only trace quantities of the hydrophosphination product were observed. Identification of the other products was unsuccessful. Compared with terminal alkynes, internal alkynes were relatively more successful substrates for hydrophosphination with **2**. Treatment of diphenylacetylene and phenylphosphine (3 eq) with 1 mol % of **2** under irradiation for 2 hours afforded 24% conversion to the vinyl product as a 7:1 ratio of *Z* : *E* isomers (Table 2). Extended reaction times appear to lead to *Z* : *E* isomerization as a 4:1 ratio is observed after 18 hours with little increase in overall yield. Vinyl phosphine

isomerization is consistent with the literature.^[14] The reaction appears to ultimately be halted by decomposition of the catalyst. Unfortunately, the trimethylsilylacetylene was unreactive in the conditions screened.

Table 2 Hydrophosphination of various substrates with **2**

Substrate	Time/h	Major product	Minor product	Conversion
2		Products unknown	100 (91 : 9)
18		Products unknown	12 (93 : 7)
23		Products unknown	100 ^{[a][b]} (97 : 3)
72		Product unknown	13 ^[f] (97 : 3)
72	None	None	0 ^[f]
26		None	4 ^{[a][e]}
Ph—	48	Products unknown		46 ^{[c][e]} (45 : 1)
24	None	None	0 ^[d]
Ph— —Ph	2	(Z/E = 7:1)	Products unknown	24 ^[e] (21 : 3)

All reactions run with 1 mol % of **2**, unless specified, and under irradiation in the near UV.

Product conversions determined by integration of ³¹P NMR spectra. Consumption of unsaturated substrate determined by integration of ¹H NMR spectra. [a] 1 equiv. unsaturated substrate: 1 equiv. phosphine. [b] Diphenylphosphine used instead of phenylphosphine. [c] 4 equiv. unsaturated substrate: 1 equiv. phosphine. [d] 1 equiv. unsaturated substrate: 2 equiv. phosphine. [e] Consumption of phosphine, determined by ³¹P NMR spectroscopy. [f] 0.1 mol % **2**.

Photoactivation versus photocatalysis was tested with an initiation experiment. Styrene and three equivalents of phenylphosphine were treated with 0.1 mol % of **2**. The reaction mixture was

irradiated for five minutes and then kept in the dark for the subsequent 18 hours. At that time, only 12% of phosphine was consumed, indicating that light is required throughout the course of the reaction and that this reactivity is photocatalysis rather than photoactivation as seen for the related iron compound, **1**. We have seen photocatalytic hydrophosphination that results from activation of a Zr–P bond.^[3], 14]

The mechanism of hydrophosphination is still under consideration, but the literature guides our thinking to an acceptable working mechanistic hypothesis. The first issue to consider is P–H bond activation. Irradiation with 360 nm light produces two equivalents of $\text{Cp}(\text{CO})_2\text{Ru}^*$, which can cooperatively cleave the P–H bond of a phosphine substrate, generating $\text{Cp}(\text{CO})_2\text{RuPRR}'$ and $\text{Cp}(\text{CO})_2\text{RuH}$, akin to compound **1**.^[3e] In the case of iron catalysis, the $\text{Cp}(\text{CO})_2\text{FeH}$ intermediate is unstable and reforms **1**, but $\text{Cp}(\text{CO})_2\text{RuH}$ is more thermally robust and hydridic.^[15] Thus, it is reasonable to suspect that $\text{Cp}(\text{CO})_2\text{RuH}$ could also react with phosphine to also form $\text{Cp}(\text{CO})_2\text{RuPRR}'$ derivatives, which are known.^[16] To test the first proposal, a stoichiometric reaction of **2** with diphenylphosphine, both $\text{Cp}(\text{CO})_2\text{RuPPh}_2$ and $\text{Cp}(\text{CO})_2\text{RuH}$ are observed by ^1H and ^{31}P NMR spectroscopy (benzene- d_6 , Eq 3).^[17] To test the latter supposition, **2** was treated with two equivalents of diphenylphosphine and monitored by NMR spectroscopy over the course of 24 hours. In that reaction, the relative concentration of $\text{Cp}(\text{CO})_2\text{RuH}$ rises and then falls with an increase in $\text{Cp}(\text{CO})_2\text{RuPPh}_2$. This observation is consistent a productive reaction of the ruthenium hydride and phosphine. However, this is a tenuous conclusion because both reaction mixtures decompose to complex mixtures over the course of 24 hours. We are confident, however, that unlike the iron system **2** is merely a precatalyst.

Next, it is important to consider P-C bond formation. Direct study in this system is problematic with the two process that lead to a phosphido intermediate (*vide supra*). The literature provides some useful indications of a likely mechanism. Rosenberg and coworkers provide excellent evidence in support for a concerted, inner-sphere (e.g., insertion) reaction of alkenes at the Ru-P bond of related indenyl ruthenium phosphido compounds.^[1h, 6a-c] That precedent provides a strong basis for a mechanistic hypothesis that involves insertion into a Ru-P bond in this system. There are limitations to that supposition, though. Rosenberg's systems, commonly (indenyl)(PPh₃)Ru=PRR', possess significantly different ligands, with respect to electronic effects, than the Cp and CO ligands of **2**. Moreover, Rosenberg's compounds are coordinately unsaturated and exhibit substantial phosphorus-to-metal π bonding.^[1h, 6a-c] The relationship between these compounds is significant nevertheless, and an insertion-based mechanism is the working hypothesis here. It is well understood that many late-metal phosphido compounds react as nucleophiles, but the observed reactivity with styrene derivatives does not support this possibility.^[18] Finally, Rosenberg has demonstrated proton transfer as a product-liberating step in a stoichiometric analogy to catalytic hydrophosphination.^[1h] That system requires a base co-catalyst to accomplish this step, but the difference in ligands between that at **2** may allow for proton transfer from these phosphine substrates, despite their modest acidity.^[19] Overall, our understanding of this system is limited, and for that reason, a proposed catalytic cycle would be too speculative to include.

Concluding remarks

UV irradiation of the commercially available compound **2** promotes efficient hydrophosphination with low catalyst loading under low intensity UV light at ambient temperature. Greater activity and expanded substrate scope were observed compared to the iron

derivative, **1**. **2** is significantly more active for hydrophosphination of alkenes with primary phosphines than previously reported iron and ruthenium compounds. Universal comparison to other reported catalysts for other substrates is difficult due to differences in substrate scope, selectivity, conditions, price, and loading. This highlights the need for benchmarking in catalysis.^[20] In particular, **2** is successful with hydrophosphination of primary phosphine substrates that have eluded **1**. In comparing diphenylphosphine, both compounds readily utilize styrene derivatives and Michael acceptors were readily reacted, but **2** is substantially more reactive. Alkynes and unactivated alkenes gave poor reactivity but support indications of an insertion-based hydrophosphination mechanism, predicted based on literature reports. More extensively studied indenyl-ruthenium compounds can do stoichiometric hydrophosphination but do not exhibit catalytic turnover.^[1h] These differences suggest that additional design and study can afford significant enhancements in iron-catalyzed hydrophosphination through tuning of **1** and other iron derivatives. That work is currently underway.

Experimental Section

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-*d*₆ was purchased from Cambridge Isotope Laboratory and then degassed and dried over NaK alloy. Diphenylphosphine was synthesized according to literature procedures and stored under an inert atmosphere of N₂ prior to use.^[21] All other reagents were acquired from commercial sources and dried by conventional means, as necessary. Proton NMR were recorded at 25 °C with a Bruker AXR 500 MHz or Varian 500 MHz spectrometer. Proton-decoupled ³¹P NMR spectra were recorded at 25 °C with a Bruker AXR 500 MHz. Resonances in ¹H NMR spectra are referenced to

the residual solvent resonance (benzene- d_6 = δ 7.16). Reported ^{31}P NMR resonances are referenced to the relevant phosphine starting material. Phenylphosphine is set to -123.0 ppm in ^{31}P NMR spectra.^[22] Diphenylphosphine and cyclohexylphosphine are set to -40.0 ppm and -111.8, respectively, in ^{31}P NMR spectra.^[22] ^[23] Spectral data for hydrophosphination products are consistent with literature reports.^[3i, 3j, 9b, 14, 21-24]

Procedure for Catalytic Experiments

For reactions with 1 mol % of **2**: In an N_2 filled dry box, 1.35 mmol of phosphine (or 0.45 mmol where applicable) and 0.45 mmol of unsaturated substrate were measured and mixed in ca. 0.5 mL benzene- d_6 . This solution was then pipetted into a scintillation vial containing 2 mg (0.0045 mmol) **2** and quickly transferred into an NMR tube wrapped with aluminum foil.

For reactions with 0.1 mol % **2** this procedure was slightly modified: The phosphine and unsaturated substrates were dissolved in ca. 0.4 mL benzene- d_6 , transferred to a foil-wrapped NMR tube, and then 0.1 mL of a 0.0045 M stock solution was syringed into the NMR tube. For both catalytic loadings, the reactions were kept in an aluminum foil wrap until initial ^1H and ^{31}P NMR spectra were acquired. After the initial NMR spectra, reactions were then placed in a Rexim G23 UV-A (9W) lamp at room temperature and shielded from ambient light. Periodic NMR spectra were collected until reactivity ceased. All reactions were performed with 0.1 mol % of **2** and 3 : 1 phosphine : unsaturated substrate, unless otherwise stated.

Acknowledgements

This work was funded by the U. S. National Science Foundation through CHE-1565658.

Dedication

Synthetic chemists continue to be inspired by the exploits of Profs. Stephen Buchwald and John Hartwig. We are delighted to share these results in celebration of their well-deserved Wolf Prize.

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