A Photoswitchable Ru cis-Dihydride Catalyst Accessed through Atypical Metal-Ligand Cooperative H₂ Activation: Photo-Enhanced Acceptorless Alcohol Dehydrogenation

Paul M. Fanara‡, Vipulan Vigneswaran†, Parami S. Gunasekera‡, Samantha N. MacMillan‡, and David C. Lacy†*

†Department of Chemistry, University at Buffalo, State University of New York; Buffalo, New York 14260, United States
‡Department of Chemistry and Chemical Biology, Cornell University; Ithaca, New York 14853, United States.

ABSTRACT: Dehydrohalogenation of pyridine-derived pincer ruthenium complexes often lead to dearomatized moieties, such as in Milstein’s PNN-Ru(CO)(Cl)(H) (1Py) catalyst. Thus, we were surprised to find an aromatized κ₃-ν,C,P binding mode in the lutidine-derived bidentate analog [{LutP}Ru(CO)(H)(PPh₃)] (2), instead of a dearomatized compound, upon dehydrohalogenation of [{LutP}Ru(CO)(Cl)(H)(PPh₃)] (1). The reaction of 2 with H₂ results in formation of a cis-dihydride [{LutP}Ru(CO)(H)₂(PPh₃)] (3) and labeling studies confirm cooperative metal-ligand activation. 3 exhibits reversible photochemistry, forming another cis-dihydride isomer (4). The liability of 4 toward ligand substitution was leveraged to demonstrate a unique example of photoswitchable H₂ production via acceptorless alcohol dehydrogenation. Labeling studies implicate metal-ligand cooperative (MLC) processes during the photocatalytic reaction, but they appear to be off-path processes based on our mechanistic study of the system. The latter emphasizes that aromatization/dearomatization may not be necessary for acceptorless transformations, which is generally consistent with several contemporary studies on analogous Ru catalysts.

INTRODUCTION

Transition metal hydrides (TMH) have rich photochemical properties. In some cases, these enable photo-assisted catalysis. Examples of these key properties include light-induced M-H homolysis, reductive elimination of H₂ from cis-dihydrides, altered chemical properties (e.g., pKₐ, hydricity, etc.), and photoisomerization (e.g., photoswitch). When these processes are chemically reversible, it benefits the system in several ways, one of which is preventing the formation of off-path generated thermodynamic sinks. However, designing reversibility into a TMH photocatalyst is not always predictable or straightforward. Phenomenologically, the cis-dihydride motif is best suited to this end because they tend to exhibit said properties.

During the course of our studies, we discovered a Ru alcohol dehydrogenation precatalyst (1) with a nominally on-path cis-dihydride complex (3) exhibiting reversible photochemical reactivity. The cis-motif was accessed through an atypical mode of metal-ligand cooperative H₂ activation by the key intermediate (2) that has unusual coordination chemistry that adds to the developing story of aromatization/dearomatization metal-ligand cooperativity (MLC) in catalytic cycles (Figure 1). Furthermore, the reversible photochemistry from 3 enabled photoswitchable H₂ production from various alcohols using very mild reagents and conditions (r.t., λ > 345 nm). The mechanism and catalysis is a unique example of a photoswitchable H₂ generation strategy with demonstrated application in the important area of acceptorless MLC alcohol dehydrogenation.

RESULTS AND DISCUSSION

In an earlier report detailing the synthesis and characterization of [{LutP}Ru(CO)(H)(Cl)(PPh₃)] (1), we briefly investigated its reaction with KOrBu and initially hypothesized a prototypical dearomatized bidentate binding mode for the product 2b analogous to 2Py (Scheme 1). However, the product exhibited unusual sensitivity to water and we did not pursue it further at the time. Since this initial study, we discovered that activation of 1 with 1 eq. K[N(SiMe₃)₂] in cold (-35 °C) and very dry...
17 of PPh3 solution to 8 equiv. of KOtBu in very dry THF, or KOtBu in very dry benzene, results in formation of a highly moisture-sensitive amber-colored species (2) (Figure 1) whose X-ray crystal structure contains a unique NCP κ3-N,C,P binding mode (Figure 2). Importantly, the κ3-N,C,P binding mode remains intact in solution as evidenced from 1H–1H ROESY NMR correlations and 1H–13C coupled HSQC NMR spectroscopy (Figures S1–S8). Analogous bindings modes and spectroscopic features have been observed in other systems,14–17 but not for ruthenium pincer complexes with pyridine-derived ligands. Ru complexes with pyridine-derived pincer ligands have deaeromatized modes such as in 2Py (Figure 1).18 The atypical binding mode in 2 imparted unique coordination chemistry and reactivity which we explore herein.

**Scheme 1. 2b, and Reaction of 2 with Excess KOtBu**

Reaction of 2 with excess KOtBu. If excess KOtBu was used to prepare 2 from 1 in THF, we noted that free PPh3 was formed along with a new species whose 1H and 31P{1H} NMR characterization is consistent with a LuP-bound Ru-OrBu anionic complex (2c) (Figures S9–S10, Scheme 1). The addition of 8 equiv. of KOtBu is required to achieve complete conversion to 2c and formation of free PPh3. The ligand substitution is reversible and solvent dependent, as removal of THF from 2c reforms 2 in essentially quantitative yield. The nature of the [Ru-OrBu] complex (2c) is not explored in detail here and has not been isolated or fully characterized as of yet, but the lability of PPh3 is an important factor in the catalysis described later.

**Reaction of 2 with Hz.** The unusual binding mode of 2 was of interest to us as we hypothesized that the Ru–C bond would be highly reactive toward H2 and H2 donors such as 2-propanol. Indeed, when a benzene solution of 2 was exposed to an atmosphere of H2, an immediate color change from amber to light yellow occurred and NMR analysis demonstrated a cis-dihydride, 3, quantitatively formed (Scheme 2). Similarly, 2 reacts quantitatively with 2-propanol to form 3 and equimolar acetone. X-ray crystallographic characterization revealed the cis-dihydride motif and 2D NMR and 1H–1H ROESY spectroscopic characterization confirms its solution-state structure is identical (Figures S11–S15). Subjecting 3 to vacuum at elevated temperatures (60 °C) or excess acetone (r.t.) resulted in no conversion to 2. More forcing conditions (110 °C) resulted in trace formation of 2 along with [(CO)(PPh3)2Ru(H2)] and other unidentified byproducts (Figure S16). This stability toward ketones and the inability to lose H2 is in contrast to previous reports with Milstein’s dihydride complex, 3Py, which spontaneously converts to 2Py with loss of H2 at room temperature.6,7,18

**Scheme 2. Reaction of 2 with H2:**

When D2 was used to prepare 3, deuterium incorporation occurs at both ruthenium and the ligand, consistent with an MLC activation of H2 (Scheme 3). The mixture of isotopomers is best represented pictorially in Scheme 3 (1H NMR, Fig. S17) and is generally consistent with what others have observed.20 Notably, H2 and HD were observed in the 1H NMR spectrum when 2 was treated with D2 indicating exchange with free dihydrogen (Figure S18). While not completely eliminated, the presence of H2 and HD was significantly reduced when light was rigorously excluded (Figures S19–S20). As such, we hypothesized that photochemical processes are responsible.

**Scheme 3. Reaction of 2 with D2:**

**Photocatalysis of 3.** We tested this hypothesis with broad-band irradiation of 3 with a Xe arc lamp (100 W) which caused a color change of the solution to orange/red.1H NMR reveals a new dihydride species (4) that slowly converts back to 3 in a few hours (Scheme 4). The 1H NMR spectrum of 4 contains two hydride resonances at -5.13 ppm (dd, J = 101, 25 Hz) and -6.09 (dd, J = 92, 17 Hz), consistent with a phosphine trans cis to each hydride (Figure S25). The 31P{1H} NMR spectrum indicates a cis conformation of the PrBu2 and PPh3 ligands, as the resonances at 77.3 ppm and 42.7 ppm are doublets with Jpp = 10 Hz and 11 Hz, respectively (Figure S26). A 1H–1H ROESY NMR of 4 shows exchange coupling between the two hydride resonances. Additionally, the hydride resonance at -6.09 ppm has a through-space coupling to one of the PrBu2 resonances at 1.30 ppm. Meanwhile the hydride resonance at -5.13 ppm has through-space coupling to the PPh3 and methyl resonances at 7.72 ppm and 2.56 ppm, respectively (Figure S27). Together with FTIR-ATR spectroscopy (Figure S28), the NMR
enables confident assignment of the structure of 4 as shown in Scheme 4.

The stability of 4 was monitored with 1H NMR spectroscopy and it quantitatively decayed with a rate of 1.90 ± 0.04 h (r.t.) back to 3 under N2 (Figures S21–S22). The decay was unaffected by static vacuum t1/2 = 1.80 ± 0.14 h (r.t.) (Figures S23–S24). When the photolysis of 3 was carried out under an atmosphere of H2, the same process occurred, except that the decay of 4 to 3 was slower (t1/2 = 3.38 ± 0.08 h) (Figures S29–S30). Additionally, when excess (10 eq) PPh3 was added to 3 prior to irradiation, no reaction occurred by 1H and 31P {1H} NMR. After a 2 h irradiation, 3 and 4 are the major products along with byproducts [(CO)(PPh3)Ru(H2)] (6), [(PPh3)3RuH] (8) (vide infra), free ligand, and other unidentified species (Figure S36) (Scheme 5). This result will be discussed later in the context of catalysis.

Scheme 4. Reversible Photochemistry of 3

Scheme 5. Summary of Decomposition Reactions of 4

The photoisomerization of 3 into 4 is unaffected by vacuum, so the conversion must be a direct photoisomerization. We can also use the results described above to determine the mechanism of isomerization of 4 back into 3. Several possibilities include a trigonal “twist”, dissociation of CO or PPh3 (or other ligand), or elimination of H2. We rule out CO loss and elimination of H2 because the rate of isomerization is unaltered when the irradiation and isomerization is performed under static vacuum. In addition, when CO is included in irradiations of 3, 4 does not form and instead a carbonylated product 8 is formed (Scheme 5, Figure S49–S51); since we do not see this byproduct in conversions between 3 and 4, the process unlikely involves CO photolysis/dissociation. For the same reasons, the loss of PPh3 is unlikely since (i) free phosphine is not observed and (ii) addition of free phosphine gave other byproducts for an otherwise clean conversion of 4 to 3. As such, we propose the isomerization is a unimolecular trigonal “twist”, but other isomerization mechanisms are plausible.

Exchange of H2 with the hydrides of 4. Irradiation of a sample of 3 under an atmosphere of D2 results in the hydride resonances washing out in the 1H NMR spectrum and reappearance in the 2H NMR spectrum. D-incorporation into the ligand was not observed (Figures S31–S32). These results suggest an exchange is taking place between the hydrides of 4 and free D2. A 1H–2H ROESY NMR spectrum of 4 under H2 confirms the exchange between both hydride resonances and free H2 (Figure S27). Variable temperature NMR and line broadening analysis furnished activation parameters of ΔH‡ = 24.0 ± 1.2 kcal·mol⁻¹ and ΔS‡ = 22.9 ± 3.4 cal·K⁻¹·mol⁻¹ (Figures S34–S35), consistent with a ligand interchange substitution between H2 and PPh3 to form proposed complex 5 (Scheme 4).

The proposed presence of 5 explains two important observations. First, the appearance of both HD and H2 when 3 or 4 was treated with D2 and exposed to light cannot be easily explained without the presence of a tetra- or tri-hydride intermediate, which are known to mediate the H2 isotope exchange reaction. Secondly, it also explains how the isomerization of 4 to 3, although not affected by vacuum, is slowed by the presence of H2; the off-path equilibrium between 4 and H2 allows for this to happen. We propose that the reaction is a ligand substitution between 4 and H2 via interchange because the broadening in the NMR spectrum is uniquely from the peaks associated with 4 and H2; although a dissociation mechanism is possible. The dissociating ligand is likely PPh3 or CO. Since we see some of the carbonylated byproduct 8 during these experiments, CO is a likely candidate.

We suspect there also a thermal reaction between H2 and 3 because if 3 and D2 are left to stand in the dark for several days, the hydride resonances eventually wash out and reappear in the 2H spectrum (Figure S33). The ligand exchange between 4 and H2 is rapid (as evidenced from the line broadening) compared to the ligand exchange between 3 and H2. This enhanced stability of 4 is important for enabling the photoswitchable catalysis.

Photoswitchable catalysis. Our previous investigation with 1 involving testing different ligand variants in alcohol dehydrogenation. In that case, and also most others, catalytic behavior was not achieved unless reactions are carried out at elevated temperatures. However, we intuited that complexes like 6 involving testing different ligand variants in alcohol dehydrogenation akin to what has been observed in certain cases. We tested several simple alcohols using 3 with irradiation from a Xe arc lamp (100 W, 345 nm cutoff filter) and achieved catalytic turnover at r.t. (Figure 3). Under the same conditions but with the exclusion of light, only substoichiometric H2 was formed (e.g., 27% H2 relative to 3 from 2-propanol; Table 1 Entry 5). A larger scale photolysis reaction was conducted open to a bubbler and resulted in comparable conversions to the closed system.

As noted, [(CO)(PPh3)RuH](H2) (6) was observed as a product when 3 was irradiated in the presence of free PPh3, and since 6 is a known alcohol dehydrogenation catalyst, we performed a control reaction but found that it was not the active catalyst. Namely, a control reaction with 6 gave 10% H2 in the dark, and

Table 1. Results of photocatalysis.

| entry | alcohol | cat, hv | carbonyl-compound + H2 | H2 relative to cata (after 12 h) |
|-------|---------|---------|-----------------------|---------------------------------|
| 1     | MeOH    | 3       | H2·CO                 | 270% (400%)                     |
| 2     | EtOH    | 3       | ethyl acetate         | 640% (1000%)                    |
| 3     | 1PhEtOH | 3       | acetylphenone         | 640% (1100%)                    |
| 4     | iPrOH   | 3       | acetonitrile          | 300% (510%)                     |
| 5     | iPrOH   | 3c     | acetonitrile          | 27%                             |
| 6     | iPrOH   | 3       | acetonitrile          | 78%                             |
| 7     | iPrOH   | 6       | acetonitrile          | 33%                             |
| 8     | iPrOH   | 7       | acetonitrile          | 28%                             |

Conditions: 2 mL of alcohol, 0.02-0.04 mol% catalyst, 200 µL benzene, under N2, irradiation with a Xe-arc lamp (100 W) with a 345 nm cutoff filter for 4 h. Yield of H2 was determined by GC. (a) average of three runs. (b) trace CO observed. (c) dark: 6 = [(CO)(PPh3)RuH](H2); 7 = [(Cl)(CO)(PPh3)2RuH]. 1PhEtOH = 1-phenylethanol.
When 3 was irradiated in C6D6 in the presence of d6-isopropanol, deuteriation occurred on the ligand (Figures S44–S45). This would seem to indicate an MLC step in the photocatalysis. However, to explain this observation, we propose that 9 or 10 may react to form 2 (or species like it), which undergoes MLC activation of alcohol in an off-path step. Hence, the MLC chemistry observed here is not likely important for turnover, as depicted in Figure 3.

Finally, we found that sub-stoichiometric H2 formed when light was excluded in reactions between 3 and 2-propanol, indicating thermal pathways are also possible when the net reaction is favored. In fact, carrying out the photolysis at elevated temperature improves the yields of H2 from isopropanol (450% at 40 °C compared to 300% at 23 °C). All of these steps are consistent with the mechanism in Figure 3.

Extension to other systems. The catalytic conversions are low compared to photocatalytic alcohol dehydrogenation with Wilkinson’s catalyst and other photocatalytic systems,25 but the conditions we used (r.t., neat alcohol, λ > 345 nm) are very mild. A notable example of mild photochemical alcohol dehydrogenation uses a platinum(II) diphosphite complex at r.t. and with visible light (λ = 410 nm), but requires a biphasic H2O and CH3Cl2 conditions and a phase transfer reagent.26 Conventional acceptorless alcohol dehydrogenation uses high temperatures27,28 or photosensitizers.28 Hence, achieving unsensitized photocatalysis H2 production (i.e. single component systems)26,27,29 at low temperatures is desirable and one possible means is to take advantage of photoswitchable cis-dihydrides and we wondered if this could be extended to other systems.

We considered that Ru-MACHO, which is a known effective alcohol dehydrogenation catalysts at low temperatures,30,31 might have photo-enhanced r.t. catalysis. Testing this hypothesis indicates that it does not. Specifically, Ru-MACHO (Ph substituted) exhibited TON ~ 6 (4 h), with or without light, for 2-propanol dehydrogenation in 4 h. This is in contrast to the work with 3, which is very slow at r.t. in the dark (TON ~0.3, 4 h, Table 1 Entry 4) compared to when irradiated to generate its more labile isomer 4 (TON = 3, 4 h, Table 1 Entry 5), effectively demonstrating the photoswitchable nature of the system.

We also tested Milstein’s Ru-PNN trans-dihydride 3Py and obtained TON = 1-3 with or without light, but 3Py is known to spontaneously lose H2 when standing in solution at r.t.,7 and we found that even the chlorido precursor to 3Py (i.e. 1Py) produces hydrogen when irradiated in anhydrous benzene, so the comparison is rather inconclusive.36 We also note that irradiation of Ru-MACHO and 3Py with broad band light resulted in solutions containing a multitude of hydride resonances in the 1H NMR spectrum and speciation by 31P{1H} NMR was complicated. Therefore, careful studies is necessary to infer the action of light on these systems which is outside the scope of this current study. Rather, our current studies on 3 and 4 provide a working hypothesis for future combined coordination and photochemical investigations, namely that photosomerizations of TMH is a new photoswitch that can be used for acceptorless alcohol dehydrogenation.

CONCLUSION

Our work with 2, having an atypical mode of MLC, provides new intermediates to consider when invoking MLC on pyridine-derived ligands. Nevertheless, our mechanistic investigation of the catalytic acceptorless alcohol dehydrogenation does not require MLC steps, consistent with a growing body of literature that has de-emphasized the importance of

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Figure 3. Proposed mechanism for photocatalysis for 2-propanol dehydrogenation. The off-path formation of 2 reforms catalyst 3 by means represented in Scheme 2 (grey).

33% when irradiated, with the hydrogen observed simply as the result of the known photoelimination of H2 from 6.26 This is not surprising as catalytic dehydrogenation from 6 requires high temperatures (110 °C).24 Likewise, (Cl)CO(PPh3)Ru(H) (7) and 1 were not catalysts.

Mechanism of photodehydrogenation. The two accepted conventional paths for acceptorless alcohol dehydrogenation are the inner sphere and outer sphere mechanisms and these have been discussed at length.13 We recently provided a rationale for a favored inner sphere path,9 consistent with other literature,27 and lately it has been recognized that MLC steps need not be involved.7 In addition the experimental results described herein, these factors influenced our mechanistic scheme (Figure 3). We recognize that the outer sphere path is also possible, but it is not discussed further.

Except for MeOH, post-irradiated solutions contain 3 and 4 as the major species indicating their overall stability in the catalytic system (Figure S48); the carbonylated byproduct 8 is a minor component (tentative structure shown in Scheme 5, Figure S49-51). We propose that the first step is the reversible photo-induced isomerization of 3 to 4. The salient component of the mechanism is the enhanced lability of PPh3 and/or CO in 4 because of the of trans-effect of the hydride ligand and/or steric crowding from the cis-diphosphite motif. The lability enhancement allows for alcohol coordination and subsequent liberation of H2 from proposed intermediate 9. Loss of H2 from 9 forms the proposed coordinatively unsaturated species 10, which is predisposed to undergo beta-hydride elimination and ligand re-coordination reforming 3; thus, the dehydrogenation is an inner sphere mechanism and no MLC steps are necessary.

We strongly suspect that the role of light in photocatalysis is only to generate 4, and not some other process. This supposition comes from our observation that the wavelength requirements for photocatalysis are the same as those required for isomerization (Fig. S46-47). It is tempting to consider a photo elimination of H2 from 3 or 4, but the isomerization of 4 back to 3 is unaffected when the entire experiment is conducted under static vacuum.
aromatization/dearomatization in catalytic cycles. The atypical MLC H₂ activation resulted in the formation of a cis-dihydride motif in 3, which in turn exhibited reversible light-induced isomerization, something that is potentially less likely on analogous trans-dihydride catalysts. The photogenerated labile compound 4 was competent to engage in catalytic r.t. alcohol dehydrogenation. Albeit, the conversions are low. Certain decomposition pathways for 4 were identified and are possible sources for the poor TON. The photo-enhanced catalysis was not observed in related Ru complexes, so we suspect that designing systems with reversible photoisomerizations (or other photochemical processes) is vital to using TMH as photoswitchable catalysts and, to our knowledge, this is the first example of photoswitchable catalysis with dihydride isomerization as the photoswitch.

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Supplementary Materials for

A Photoswitchable Ru cis-Dihydride Catalyst Accessed through Atypical Metal-Ligand Cooperative H₂ Activation: Photo-Enhanced Acceptorless Alcohol Dehydrogenation

Paul M. Fanara, Vipulan Vigneswaran, Parami S. Gunasekera, Samantha N. MacMillan, and David C. Lacy*

Correspondence to: dclacy@Buffalo.edu

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Figure S36. 300 MHz $^1$H NMR of a solution of 3 and 10 equiv. PPh$_3$ in C$_6$D$_6$ after 2 h of broadband irradiation at 23 °C zoomed in on the hydride region. Unlabeled peaks are unknown products.

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Figure S38. 300 MHz $^1$H NMR spectra of a solution of 0.00310 mmol of 3 in C$_6$D$_6$ with 0.0931 mmol of 1-phenylethanol before irradiation (bottom), after 7 h of irradiation with a 345 nm cutoff filter (middle), and after spiking the sample with 1 µL of acetophenone.
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Figure S40. 500 MHz $^1$H NMR spectra of the hydride region of a solution of 0.0030 mmol of 3 in CD$_3$OD before irradiation (bottom) and after 6 h of irradiation with a 345 nm cutoff filter (top).

Figure S41. QE-GCMSMS headspace mass spectrum (above) and chromatogram (below) of an aliquot (10 µL) of a solution of 3 in methanol after 5 h of irradiation with a 345 nm cutoff filter at 23 °C. A broad peak at 1.50 minutes corresponded to a mass of 30.0101 amu which is in agreement to the formula CH$_2$O ($M_{\text{calc'd}} = 30.0106$) with a 1.46 ppm error.

Figure S42. Direct injection (10 µL) of an aliquot of a solution of 3 in methanol after 5 h of irradiation with a 345 nm cutoff filter at 23 °C, exposed to ambient atmosphere, into a QE-LCMSMS (above) showed a peak consistent with the formula, Ru(H)(LutP)(CO) ($[M+]_{\text{calc'd}} = 382.0868$; $[M+]_{\text{found}} = 382.0862$) and consistent with calculated isotopic distribution (below). A second peak consistent with carbonylation was observed ($[M+CO]_{\text{calc'd}} = 410.0817$; $[M+CO]_{\text{found}} = 410.0811$). In addition, peaks with masses consistent with oxidized LutP and triphenylphosphine were observed in the mass spectrum.

Figure S43. 300 MHz $^1$H NMR spectra of a solution of 0.046 mmol of 3 in C$_6$D$_6$ and 0.057 mmol of paraformaldehyde before irradiation (bottom), after 4 h of irradiation with a 345 nm cutoff filter (middle), and after 6 h of irradiation with a 345 nm cutoff filter and left overnight in ambient light (top).

Figure S44. (top) 500 MHz $^1$H NMR spectrum of a solution of 3 in C$_6$D$_6$ and 2-propanol-d$_8$. (bottom) The same solution after 1.5 h of broadband irradiation at 23 °C. (left) Zoomed in on the H$_2$, HD, and $\delta$CH$_2$ regions. (right) Zoomed in on the hydride region.

Figure S45. 500 MHz $^2$H NMR spectrum of a solution of 3 in C$_6$H$_6$ (spiked with C$_6$D$_6$) and 2-propanol-d$_8$ after 1.5 h of broadband irradiation at 23 °C.

Figure S46. GC trace (zoomed in on the H$_2$ region) of the headspace samplings of a solution of 3 in 2-propanol after 1 h of irradiation at 23 °C with a 345 nm (black), 420 (blue), or 515 nm (green) cutoff filter.

Figure S47. 300 MHz $^1$H NMR of a solution of 3 in C$_6$D$_6$ before irradiation (bottom) and after 1 min of irradiation at 23 °C with a 515 nm cutoff, 420 nm cutoff, 345 nm cutoff, and UV band pass filter.

Figure S48. 300 MHz $^1$H NMR spectrum of a solution of 3 and ethanol in C$_6$D$_6$ after 4.5 h of irradiation with a 345 nm cutoff filter zoomed in on the hydride region. The same species were observed for 2-propanol and 1-phenylethanol; note for methanol, these species were not observed.

Figure S49. 300 MHz $^1$H NMR spectrum of a solution of 3 under an atmosphere of N$_2$(g) (bottom), and CO(g) (top) in C$_6$D$_6$ after 1 h of broadband irradiation.

Figure S50. 121 MHz $^{31}$P NMR spectrum of a solution of 3 under an atmosphere of N$_2$ (bottom), and CO(g) (top) in C$_6$D$_6$ after 1 h of broadband irradiation.

Figure S51. Drop-cast FTIR-ATR spectrum of 3 under CO(g) after 1 h of broadband irradiation.
Figure S52. Overlayed UV-vis spectra of complex 2 (0.182 mM, red) and 3 (0.25 mM, black).

Table S1. Crystal data and structure refinements for 2 and 3.

References
METHODS AND MATERIALS

• General Methods. Chemicals were obtained from commercial vendors unless otherwise noted. All manipulations of oxygen sensitive compounds were performed under an argon atmosphere with standard Schlenk techniques or under nitrogen in a VAC Atmosphere Genesis Glovebox. Complex 1 was prepared according to literature. Ru-MACHO (Ph, chloride complex) was converted into the dihydride following literature methods. Anhydrous organic solvents were sparged with argon and purified using a Pure Process Technology solvent purification system and were stored over 3 Å molecular sieves before use. Molecular sieves were activated at 200 °C under vacuum (< 100 mTorr) for 3-4 days prior to use. Deuterated solvents were degassed via three freeze-pump-thaw cycles and stored over sieves in a glovebox. Solvents for syntheses of and manipulations involving 2 were further dried by passing over a plug of dry basic alumina on a medium fritted glass funnel in a glovebox and used immediately. Basic alumina was dried at 200 °C under vacuum (< 100 mTorr) for 2-3 days prior to use. NMR spectra were collected on a Varian Mercury-300 MHz, Inova-400 MHz, or an Inova-500 MHz spectrometer. FTIR-ATR spectra were collected inside of a VAC Atmospheres Genesis glovebox using a Bruker Alpha IR spectrometer with the “ATR Platinum” insert adapter (diamond crystal). Headspace analysis was obtained using a PerkinElmer Clarus 580 GC. High resolution mass spectrometry of 3 was conducted in MeOH using an FTICR Bruker 12 T mass spectrometer. Headspace GC-MS analysis for MeOH dehydrogenation product identification was performed on a Thermo Scientific Q-Exactive Liquid Chromatograph Orbitrap Mass Spectrometer (QE-LCMSMS) equipped with a TG-5SILMS, 30 m x 0.25 mm chromatographic column from Thermo Fisher Scientific. LC-MS analysis of reaction mixtures was performed on a Thermo Fisher Q-Exactive Liquid Chromatograph Orbitrap. Tandem Mass Spectrometer (QE-LCMSMS). T1 measurements were recorded on a Varian Mercury-300 MHz, Inova-400 MHz instrument using the inversion recovery method according to literature. The reported T1 (min) are the lowest T1 observed between 298-183 K in THF-d8 (3) or C7D8 (4).

• Crystallographic Methods. Low-temperature X-ray diffraction data for Rlacy87 (2) (CCDC 2091357) and Rlacy86 (3) (CCDC 2091358) were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hpxip detector with either Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54184 Å), from a PhotonJet micro-focus X-ray source at 100 K and 104 K, respectively. The diffraction images were processed and scaled using the CrysAlisPro software. The structures were solved through intrinsic phasing using SHELXT and refined against F2 on all data by full-matrix least squares with SHELXL following established refinement strategies. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. Hydrogen atoms bound to ruthenium were located in the difference Fourier synthesis and subsequently refined freely. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Table S1.

• General Photochemistry Methods. All photolysis experiments were carried out in sealed vessels, which were positioned 2” away from the aperture of a 100 W xenon-arc lamp (Newport INC.; APEX2). Various filters were employed with the xenon arc lamp: no filter (i.e., broadband), UV band pass filter (50% Abs Cutoff = 382 nm; %Tavg ≥ 70% = 300 – 375 nm; %Tavg ≤ 1% = 400 –
635 nm; \%T_{\text{avg}} \leq 10\% = 280 – 290 nm), a 345 nm cutoff filter (\(\lambda \geq 345\) nm), a 420 nm cutoff filter (\(\lambda \geq 420\) nm), and a 512 nm cutoff filter (\(\lambda \geq 512\) nm). Temperature control was achieved by immersing the Schlenk tubes in water contained in a water-cooling jacket set to the desired temperature.

**Photocatalysis.** In a N\(_2\) filled glovebox, 200 \(\mu\)L of a stock solution of complex 3 (0.04 M) in dry benzene was added to a 50 mL Schlenk tube along with a stir bar. The specified alcohol was dried over basic alumina (1-phenylethanol and isopropanol) or 3 Å molecular sieves for at least 2 days (methanol and ethanol) before 2.0 mL was added to the tube. The final concentration of catalysts was 0.004 M. The Schlenk tube was then sealed with a rubber septum, taken out of the glovebox, and irradiated at 23 °C. Each alcohol was performed in triplicate, except when H\(_2\) yields were below 100%. The overnight experiments for each alcohol were sampled after 4 h and again after 12 h. Note, 3 has poor solubility in neat alcohols. Irradiations of 3 in neat alcohols resulted in homogeneous solutions during the course of irradiation (except for MeOH), and the yields of H\(_2\) for each alcohol were comparable (sometimes slightly higher) to those that used benzene stock solutions of 3.

**H\(_2\) Quantification from Photocatalysis.** H\(_2\) quantification was achieved by removing 3 mL of headspace with a gas-tight syringe and analyzed using gas chromatography. The area of the H\(_2\) peak was compared to a calibration curve to determine the percent H\(_2\) in the headspace.

**Determination of organic products from the photolysis of 3 in methanol, ethanol, and 1-phenylethanol.** In a N\(_2\)-filled glovebox, a stock solution of 3 in C\(_6\)D\(_6\) (0.0062 M) was prepared. Approximately 0.500 mL (0.00310 mmol, 1 equiv.) was transferred by glass syringe to an NMR tube equipped with J-Young valve. The alcohol (0.155 mmol, 50 equiv. for methanol and ethanol; 0.0931 mmol, 30 equiv. for 1-phenylethanol) was subsequently added by glass syringe. An initial \(^1\)H NMR spectra was collected, and the tube was subsequently irradiated with a 100 W Xe arc lamp through a 345 nm cut off filter. \(^1\)H NMR spectra were collected 2, 4.5 and 23 hours after initial photolysis for methanol and ethanol; for 1-phenylethanol photolysis was stopped after 7 hours and spectra was collected at this time. After 23 hours, compound 4 was still present in the sample containing ethanol whereas in the sample containing methanol the only identifiable product was the carbonylated product 8. In the ethanol experiment, ethyl acetate resonances were present after photolysis and were observed to grow in over time. The presence of ethyl acetate was confirmed by spiking this sample with 1 \(\mu\)L of dry ethyl acetate (Fig. S37). For 1-phenylethanol, peaks characteristic of acetophenone were observed and confirmed by spiking this sample with 1 \(\mu\)L of dry aceto phenone (Fig. S38).

**Determination of organic products from the photolysis of 3 in 2-propanol (large scale).** 3 mL of a 0.005 M 2-propanol solution of 3 was irradiated for 19 h (broadband). The apparatus was attached to a bubbler to vent H\(_2\). To quantify acetone, the post-irradiated mixture was measured into a graduated cylinder and treated with standard (hexamethyldisiloxane) and an aliquot was dissolved in CDCl\(_3\) and analyzed by \(^1\)H NMR spectroscopy. The yield of acetone was 700% relative to 3.

**Determination of organic products from the photolysis of 3 in 2-propanol (small scale).** An NMR tube equipped with a J-Young valve was charged with 0.400 mL of a solution of 3 in C\(_6\)D\(_6\)
(0.012 M) in a N2-filled glovebox. Dry 2-propanol (0.097 mmol, 20 equiv.) was added via glass syringe to the tube. Initial spectra were collected before photolysis and then subsequently collected at 4, 6 and 12 hours after irradiation. After 12 hours, the single characteristic peak of acetone was observed to grow in and was confirmed by spiking this sample with 1 µL of acetone (Fig. S39).

**Additional determination of organic products from the photolysis of 3 in neat CD$_3$OD.** In a N$_2$-filled glovebox, compound 3 (2.0 mg, 0.0031 mmol) was suspended in 0.500 mL of CD$_3$OD in a tared vial (Note: 3 is only partially soluble in methanol). This suspension was transferred to a J-Young NMR tube and $^1$H and $^2$H NMR spectra were obtained. The initial $^1$H NMR spectrum shows the presence of HD and H$_2$. After irradiation for a period of an hour, the hydridic resonances of 3 and 4 were not observed. Subsequent irradiation for 5 hours revealed a signal characteristic of carbonylated species 8 as determined by $^1$H NMR (Fig. S40).

**Mass spectrometric analysis of products from the photolysis of 3 in methanol.** In a N$_2$-filled glovebox, a 20 mL headspace GC vial was charged with 1.000 mL of methanol and 50 µL of a benzene solution of 3 (0.04 M). A stir bar was placed in the vial and was subsequently irradiated with a 100 W Xe arc lamp with a 345 nm cutoff filter for a period of 4 hours. Headspace GC-MS analysis using selective ion-monitoring showed the presence of formaldehyde (Fig. S41). Positive mode LC-MS analysis of the reaction mixture revealed the presence of signals consistent with [\{LutP\}Ru(H)(CO)]$^+$ and [\{LutP\}Ru(H)(CO)$_2$]$^+$ (Fig. S42).

**Photolysis of 3 with paraformaldehyde.** To test the effects of formaldehyde in irradiations of 3 we performed the following experiment. In a N$_2$-filled glovebox, paraformaldehyde (1.7 mg, 0.057 mmol, 12 equiv.) was added to a solution of 3 (3.0 mg, 0.046 mmol, 1 equiv.) in 0.400 mL of C$_6$D$_6$ in a vial (Note: paraformaldehyde is not soluble in C$_6$D$_6$). The suspension was transferred to a J-Young NMR tube. Initial $^1$H NMR spectrum, prior to photolysis, revealed the presence of H$_2$ indicating formaldehyde dehydrogenation. The tube was irradiated for 4 hours and a $^1$H NMR spectrum was collected. The only hydridic signals observed were from carbonylated species 8, the same product obtained when 3 was irradiated under CO in C$_6$D$_6$. Additionally, other organic products, including methanol and some aldehydic species were observed (Fig. S43). Collectively, this indicates that 3 also dehydrogenates formaldehyde.

**Synthesis of Compounds**

**Synthesis of (CO)(H)(PPh$_3$)($\kappa^2$-$N,C,P$-LutP$^-$$) ruthenium(II) (2)**

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**K[N(SiMe$_3$)$_2$] Method.** In a N$_2$-filled glovebox, a 20 mL scintillation vial with a stir bar was charged with freshly dried THF (4 mL) and 1 (50.0 mg, 0.0736 mmol). This mixture was stirred until homogeneous. The solution was subsequently cooled to -35 °C in a cold-well before
K[N(SiMe$_3$)$_2$] (14.6 mg, 0.0736 mmol) was added. Upon addition of K[N(SiMe$_3$)$_2$], the solution became an amber color. The solution was stirred for 5 minutes at -35 °C. The amber solution was then removed from the cold-well and the solvent was removed in vacuo. The remaining residue was treated with dry diethyl ether (5 mL). The resulting amber suspension was filtered and the solids were washed with diethyl ether until the filtrate was colorless. Solvent was then removed from the filtrate in vacuo to yield an amber-brown solid (43.0 mg, 91%). Amber crystals suitable for diffraction were grown from diethyl ether at -35 °C.

**KOtBu Method.** In a N$_2$-filled glovebox, a 20 mL scintillation vial with a stir bar was charged with freshly dried benzene (2 mL) and 1 (20.0 mg, 0.0294 mmol). This mixture was stirred until homogeneous. Subsequently, KOtBu (3.6 mg, 0.032 mmol) was added to the stirring pale-yellow solution at room temperature. Upon addition of KOtBu at room temperature, the solution became an amber color. The solution was stirred for a further hour at room temperature during which a white solid (KCl) formed. After an hour had passed the amber mixture was filtered and solvent was removed in vacuo leaving an amber-brown solid behind. To this residue dry diethyl ether (5 mL) was added, and the resulting amber suspension was filtered. The remaining solid residue was washed with diethyl ether until the filtrate was colorless. Solvent was then removed from the filtrate in vacuo to yield an amber-brown solid (18.0 mg, 95%).

**NOTE:** Compound 2 is extremely water sensitive as well as thermally unstable and must be stored at -35 °C or used immediately after isolation. Thus, HRMS analyses were unsuccessful.

Spectroscopic Data for 2: $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 7.74 (m, 6H, P(o-(C$_6$H$_5$)$_3$)), 7.00 (m, 9H, P(m,p-(C$_6$H$_5$)$_3$)), 6.59 (t, $J = 8$ Hz, 1H, py), 5.83 (vt, $J = 9$ Hz, 2H, py), 1.78 (d, $J = 3$ Hz, 1H, CHP), 1.70 (s, 3H, CH$_3$), 1.40 (d, $J = 14$ Hz, 9H, P(CH$_3$)$_3$)$_b$, 1.14 (d, $J = 14$ Hz, 9H, P(CH$_3$)$_3$)$_a$, -14.16 (dd, $J = 23$, 19 Hz, 1H, RuH). $^1$H NMR (300 MHz, C$_7$D$_8$): $\delta$ 7.83 – 7.65 (m, 6H, P(o-(C$_6$H$_5$)$_3$)), 7.15 – 6.97 (m, 9H, P(m,p-(C$_6$H$_5$)$_3$)), 6.67 (t, $J = 8$ Hz, 1H, py), 5.92 (d, $J = 8$ Hz, 1H, py), 5.86 (d, $J = 8$ Hz, 1H, py), 1.79 (d, $J = 3$ Hz, 1H, CHP), 1.74 (s, 3H, CH$_3$), 1.44 (d, $J = 13$ Hz, 9H, P(CH$_3$)$_3$)$_b$, 1.19 (d, $J = 13$ Hz, 9H, P(CH$_3$)$_3$)$_a$, -14.21 (dd, $J = 23$, 19 Hz, 1H, RuH). $^{31}$P$_2$$^1$H NMR (121 MHz, C$_6$D$_6$): $\delta$ 118.00 (d, $J = 234$ Hz, P(tBu)$_2$), 54.77 (d, $J = 233$ Hz, P(Ph)$_3$). $^{31}$P NMR (121 MHz, C$_6$D$_6$): $\delta$ 118.33 (dd, $J = 235$, 5 Hz, P(tBu)$_2$), 54.87 (dd, $J = 235$, 7 Hz, PPh$_3$). $^{13}$C $^1$H NMR (75 MHz, C$_6$D$_6$): $\delta$ 211.52 (CO), 168.55 (d, $J = 2.8$ Hz, py), 157.72 (py), 139.02 (d, $J = 34.3$ Hz, P(C$_6$H$_5$)$_3$), 134.18 (py), 134.07 (d, $J = 12.3$ Hz, P(o-(C$_6$H$_5$)$_3$)), 128.83 (P(C$_6$H$_5$)$_3$), 127.94 (P(C$_6$H$_5$)$_3$), 117.00 (py), 113.50 (d, $J = 3.4$ Hz, py), 36.14 (dd, $J = 13.2$, 8.8 Hz, P(C$_6$H$_5$)$_3$)$_a$, 35.09 (d, $J = 25.6$ Hz, P(C$_6$H$_5$)$_3$)$_b$, 31.65 (d, $J = 6.1$ Hz, P(C$_6$H$_5$)$_3$)$_a$, 30.95 (d, $J = 4.1$ Hz, P(C$_6$H$_5$)$_3$)$_b$, 22.25 (CH$_3$), 12.41 (dd, $J = 6.8$, 4.5 Hz, CHP). FTIR-ATR: 1880 cm$^{-1}$ (v$_{CO}$).

- **Synthesis of (CO)-cis-(H)$_2$-trans-(PPh$_3$) (κ$^2$N,P-LutP)ruthenium(II) (3)**

\[ \text{Ph}_3\text{P} + \text{Ru}(\text{tBu})_2 \]

\[ \rightarrow \text{Ph}_3\text{P} + \text{Ru}(\text{tBu})_2 \]

3
**Dihydrogen Method.** In a N₂-filled glovebox, an oven-dried Schlenk flask equipped with a stir bar was loaded with I (80.0 mg, 0.118 mmol). Freshly dried THF (10 mL) was added, and the mixture was stirred until the solid was fully dissolved to yield a pale-yellow solution. To the Schlenk flask, a solid addition arm loaded with K[N(SiMe₃)₂] (23.5 mg, 0.118 mmol) was equipped. The flask was sealed and brought out of the glovebox and attached to a Schlenk line. The solution was subjected to three freeze-pump-thaw cycles and then brought under an atmosphere of dihydrogen (1 atm) at room temperature and stirred for 10 minutes. K[N(SiMe₃)₂] was then dispensed into the flask in one portion. Color changes were noted over a period of 10 minutes from pale-yellow to dark-yellow and finally to amber. The amber solution was allowed to stir for another hour under dihydrogen. Subsequently, solvent was removed in vacuo to yield an amber residue. The Schlenk flask was brought back into the glovebox and the residue was dissolved in dry benzene and filtered into a tared scintillation vial. The solution was placed in a freezer at -35 °C for a period of 20 minutes and then lyophilized over a period of 2 hours to yield a pale-yellow, fluffy solid that was identified as the title compound (66 mg, 87%). Pale-yellow crystals were grown from layering a solution of 3 under hexane at -35 °C.

NOTE: Compound 2 can also be prepared independently and subjected to direct addition of H₂. However, owing to the high-moisture sensitivity of 2, it is advised to access 2 in situ to avoid decomposition products that are difficult to separate from the final product, 3.

**Isopropanol Method.** A J-Young NMR tube was charged with a solution of 2 (8.0 mg, 0.012 mmol) in freshly dried C₆D₆ (0.75 mL). Degassed, freshly dried 2-propanol (3.1 μL, 0.041 mmol) was added to this solution via glass syringe. An NMR of the resulting solution 15 min after addition of 2-propanol revealed a mixture of 3, excess 2-propanol, and acetone in a 1:2.3:1 ratio.

Spectroscopic Data for 3: ¹H NMR (300 MHz, C₆D₆): δ 7.93 – 7.75 (m, 6H, P(o-(C₆H₅)₃)), 7.13 – 6.91 (m, 9H, P(m,p-(C₆H₅)₃)), 6.78 (t, J = 8 Hz, 1H, py), 6.58 (d, J = 8 Hz, 1H, py), 6.29 (d, J = 8 Hz, 1H, py), 3.51 (dd, J = 16, 6 Hz, 1H, CH₂P), 3.23 (ddd, J = 16, 9, 4 Hz, 1H, CH₂P), 2.51 (s, 3H, CH₃), 1.39 (d, J = 13 Hz, 9H, P(C(CH₃)₃)), 1.11 (d, J = 12 Hz, 9H, P(C(CH₃)₃)), -5.69 (dddd, J = 38, 22, 6, 4 Hz, 1H, RuH), -15.59 (dddd, J = 31, 17, 6 Hz, 1H, RuH). ¹³C{¹H} NMR (121 MHz, C₆D₆): δ 108.7 (d, J = 251 Hz, P(rBu₂)), 59.4 (d, J = 253 Hz, PPh₃). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ 210.47 (CO), 163.71 (dd, J = 5.0, 1.9 Hz, py), 162.97 (py), 141.98 (d, J = 37.6 Hz, P((C₆H₅)₃)), 134.54 (py), 134.11 (d, J = 11.5 Hz, P(o-(C₆H₅)₃)), 128.59 – 128.37 (m, P(C₆H₅)₃), 127.74 (P(C₆H₅)₃), 121.47 (py), 119.32 (d, J = 7.3 Hz, py), 41.50 (d, J = 16.0 Hz, CH₂P), 36.59 (t, J = 2.9 Hz, P(C(CH₃)₃)), 33.58 (d, J = 19.0 Hz, P(C(CH₃)₃)), 31.89 (d, J = 5.9 Hz, CH₃), 31.68 (d, J = 4.9 Hz, P(C(CH₃)₃)), 29.35 (d, J = 5.9 Hz, P(C(CH₃)₃)). FTIR-ATR: 1901 cm⁻¹ (ν(CO)). HRMS (FT-ICR-MS): [(C₃H₂₆NP)(PPh₃)(CO)(H₂)Ru]⁺ ([M-H]⁺); m/z (found) = 644.176504; m/z (calcd) = 644.177959. T₁(min@400 Hz): 315 ms (-5.69 ppm, 223 K, C₇D₈) and 421 ms (-15.60 ppm, 213 K, C₇D₈).

- Characterization of (CO)-cis-(H)₂-cis-(PPh₃)(κ²-N,P-LutP) ruthenium(II) (4)
**Synthesis from 2.** A J-Young NMR tube was charged with a solution of 2 (10 mg, 0.016 mmol) in dry C₆D₆ (~0.5 mL) in a N₂-filled glovebox. This tube was subjected to three freeze-pump-thaw cycles, after which the headspace was charged with dihydrogen (1 atm, r.t) to give a yellow-orange solution. After 15 min a ¹H NMR spectrum was taken to confirm complete conversion to 3. Once the conversion was complete by NMR, the tube was irradiated with a 100 W xenon-arc lamp with no filter (i.e., broadband irradiation) in a 23 °C water bath for 1 h. A ¹H NMR spectrum taken after irradiation was ceased (~5-10 min) indicates an ~80:20 ratio of 4:3. Complex 4 converts cleanly back to 3 over the course of 12 h.

**Synthesis from 3.** A J-young tube was charged with a solution of 3 (9.5 mg, 0.016 mmol) in dry C₆D₆ (~0.5 mL) in a N₂-filled glovebox. This solution was irradiated with a 100 W xenon-arc lamp with no filter in a 23 °C water bath for 1 h. A ¹H NMR spectrum taken after irradiation was ceased (~5-10 min) indicates an ~80:20 ratio of 4:3. Note: Photolysis of 3 in THF-d₈ resulted in degradation products.

**Spectroscopic Data for 4:** ¹H NMR (500 MHz, C₆D₆): δ 7.77 – 7.64 (m, 6H, P(o-(C₆H₅)₃)), 7.12 – 6.98 (m, 9H, P(m,p-(C₆H₅)₃)), 6.59 (t, J = 8 Hz, 1H, py), 6.38 (d, J = 8 Hz, 1H, py), 6.16 (d, J = 8 Hz, 1H, py), 3.06 (dd, J = 16, 8 Hz, 1H, CH₂P), 2.76 (dd, J = 17, 5 Hz, 1H, CH₂P), 2.56 (s, 3H, CH₃), 1.30 (d, J = 12 Hz, 9H, P(C(CH₃)₃)₉), 1.11 (d, J = 13 Hz, 9H, P(C(CH₃)₃)₉), -5.14 (dd, J = 101, 25 Hz, 1H, RuH), -6.10 (dd, J = 92, 17 Hz, 1H, RuH). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 77.92 (d, J = 11 Hz, P(tBu)), 42.69 (d, J = 11 Hz, PPh₃). FTIR-ATR: 1886 cm⁻¹ (νCO). T₁(min@400 Hz): 349 ms (~5.14 ppm, 243 K, C₇D₈) and 391 ms (~6.03 ppm, 243 K, C₇D₈).

**Characterization of 2c (tentative structure shown)**

**Reaction of 2 with excess KOtBu (2c).** When more than one equivalent of KOtBu was used in the synthesis of 2 from 1, free PPh₃ and an anionic {LutP}Ru(OtBu) complex (2c) was formed in addition to 2 (Figs. S9(top)–S10(top)). The reaction of 2 with one equiv. of KOtBu and one equiv. of 18-crown-6 gave complete conversion to 2c and other unidentified byproducts (Figs. S9 (bottom)–S10 (bottom)). Attempts to isolate 2c have so far been unsuccessful.
Spectroscopic data for 2c: $^1\text{H}$ NMR (500 MHz, THF-$d_6$) $\delta$ 6.28 (t, $J = 8$ Hz, 1H, py), 5.90 (d, $J = 9$ Hz, 1H, py), 5.21 (d, $J = 6$ Hz, 1H, py), 3.10 (s, 1H, CHP), 2.19 (s, 3H, CH$_3$), 1.37 (d, $J = 12$ Hz, 9H, P(C(CH$_3$)$_3$)$_3$), 1.32 (s, 9H, O(C(CH$_3$)$_3$)). 1.15 (d, $J = 13$ Hz, 9H, P(C(CH$_3$)$_3$)$_3$)$_6$, -19.14 (d, $J = 36$ Hz, 1H, RuH). $^{31}\text{P}$ NMR (202 MHz, THF-$d_6$) $\delta$ 120.74 (d, $J = 24$ Hz, $P$(tBu)$_2$).

**Reactions involving deuterium (D$_2$ and 2-propanol-$d_8$)**

**Reaction of 2 with D$_2$.** A solution of 2 (10 mg, 0.016 mmol) in dry C$_6$D$_6$ ($\sim$0.5 mL) was added to a J-young tube in a N$_2$-filled glovebox. This tube was subjected to three freeze-pump-thaw cycles, after which the headspace was charged with D$_2$ (1 atm, r.t). A $^1\text{H}$ NMR spectrum was taken. The tube was then brought back into the glovebox, transferred to a 20 mL scintillation vial, and the solvent was removed in vacuo. The residue was dissolved C$_6$H$_6$ ($\sim$0.5 mL) and C$_6$D$_6$ ($\sim$5 µL) and transferred to a new J-Young tube before a $^2\text{H}$ NMR spectrum was taken.

After 1 h under ambient light (Figs. S17–S18), the $^1\text{H}$ and $^2\text{H}$ NMR spectra indicate deuterium incorporation at both the ruthenium center and the methylene arm of the ligand. Two hydride/deuteride isotopomers are observed in a 1:1 ratio with minor shoulders with are suspected to be the diastereomers of these major complexes. In the absence of light these minor peaks are not observed, indicating that light is involved in the isomerization process (Figs. S19–S20).

Note: H$_2$ and HD were observed in the $^1\text{H}$ NMR spectrum when 2 was treated with D$_2$ indicating exchange with free dihydrogen in the presence of light (Figs. S17–S18). In the absence of light only trace amounts of H$_2$ and HD were detected by NMR (Figs. S19–S20).

**Reaction of 3 with D$_2$.** A solution of 3 (10 mg, 0.016 mmol) in dry C$_6$D$_6$ ($\sim$0.5 mL) was added to a J-Young tube in a N$_2$-filled glovebox. This tube was subjected to three freeze-pump-thaw cycles, after which the headspace was charged with D$_2$ (1 atm, r.t). A $^1\text{H}$ NMR spectrum was taken. The tube was then brought back into the glovebox, transferred to a 20 mL scintillation vial, and the solvent was removed in vacuo. The residue was dissolved C$_6$H$_6$ ($\sim$0.5 mL) and C$_6$D$_6$ ($\sim$5 µL) and transferred to a new J-Young tube before a $^2\text{H}$ NMR spectrum was taken.

With $\sim$1 h of broadband irradiation with a 100 W xenon-arc lamp (Figs. S31–S32) or $\sim$4 days in the dark (Fig. S33), $^1\text{H}$ and $^2\text{H}$ NMR spectra indicate nearly complete incorporation of deuterium into both hydride resonances. Importantly, no incorporation in the ligand was observed.

Note: H$_2$ and HD were observed in the $^1\text{H}$ NMR spectrum when 3 was treated with D$_2$ indicating exchange with free dihydrogen when irradiated (Figs. S31–S32). In the absence of light only trace amounts of H$_2$ and HD were detected by NMR (Fig. S33).

**Reaction of 3 with 2-propanol-$d_8$.** A solution of 3 (9.25 mg, 0.0143 mmol), 2-propanol-$d_8$ (2.2 µL, 0.029 mmol) in dry C$_6$D$_6$ ($\sim$0.5 mL) J-young tube N$_2$-filled glovebox. This tube was irradiated with a 100 W xenon-arc lamp with no filter in a 23 °C water bath for $\sim$1.5 h. A $^1\text{H}$ NMR spectrum (Fig. S44) was taken. The tube was then brought back into the glovebox, transferred to a 20 mL scintillation vial, and the solvent was removed in vacuo. The residue was dissolved C$_6$H$_6$ ($\sim$0.5 mL) and C$_6$D$_6$ ($\sim$5 µL) and transferred to a new J-Young tube before a $^2\text{H}$ NMR spectrum was taken (Fig. S45).

With $\sim$1.5 h of irradiation, $^1\text{H}$ and $^2\text{H}$ NMR spectra clearly show incorporation of deuterium into the ligand methylene arm (Figs S44–S45).
• **Wavelength required for H₂ production from 2-propanol and 3.** A solution of 3 (10 mg, 0.016 mmol) in 2-propanol (2.0 mL) was added to a 50 mL Schlenk tube in an N₂-filled glovebox. This tube was sealed with an unpunctured septa and secured with electrical tape before bringing out of the glovebox. The tube was irradiated with a 100 W xenon-arc lamp for 1 h at 23 °C using a 520 nm cutoff filter before the headspace was sampled and analyzed for H₂ by gas chromatography. This was repeated using 420 nm and 345 nm cutoff filters. The 512 nm and 420 nm filters yielded nominal H₂ while the 345 nm cutoff filter yielded significantly more H₂ (Fig. S46).

• **Wavelength required for photoisomerization of 3 to 4.** To determine the wavelength of light required to isomerize 3 to 4, a solution of 10 mg 3 (10 mg, 0.016 mmol) in dry C₆D₆ (0.5 mL) was added to a J-Young NMR tube in an N₂-filled glovebox. This tube was sealed, brought out of the glovebox, and photolyzed for 1 min at 23 °C using a filter before a ¹H NMR spectrum was taken to determine the ratio of 4 to 3. A 515 nm cutoff filter, a 420 nm cutoff filter, a 345 nm cutoff filter, and a UV band pass filter were used. Very little conversion to 4 was observed for the 515 nm cutoff filter (~2%), 420 nm cutoff filter (~7 %), and UV band pass filter (~5%). The 345 nm cutoff filter yielded significant conversion to 4 (~24%) (Fig. S47).

• **Other byproducts from irradiation of 3.**

*Summary of byproducts observed.* In some cases, when less than pristine samples of 3 were irradiated under H₂ for long periods of time, [(PPh₃)₃Ru(H)₄] (Fig. S36), [(CO)(PPh₃)₃Ru(H)₂] (6) (Fig. S36), and carbonylated byproduct 8 were observed (Figs. S49-S51)

**Carbonylated product (8): irradiation of 3 under CO.** An NMR sample of 3 (6.7 mg, 0.010 mmol) in C₆D₆ (0.450 mL) was prepared in a nitrogen filled glovebox and quantitatively transferred to a J-Young tube. The tube was removed from the glovebox and then connected to a Schlenk line and subjected to three freeze-pump-thaw cycles. After the tube had returned to room temperature, CO (10% in Ar, 1 atm) was introduced to the sample for a period of two minutes. The tube was inverted and shaken and subsequently irradiated with broadband light for one hour. The sample was then quickly analyzed by ¹H and ³¹P {¹H} NMR spectroscopy with no further isolation or purification (Figs. S49-S51). The major product (8) contains ¹H and ³¹P {¹H} NMR resonances which suggest a carbonylated product in which the pyridine ring of LutP has dissociated and substituted with a CO ligand. When 8 was prepared for an overnight ¹³C NMR experiment, other products (from a multitude of ¹³C signals) and free H₂ were observed in a subsequent ¹H NMR experiment suggesting that 8 is not indefinitely stable under an atmosphere of CO and precluded its isolation for definitive characterization. Complex 8 is also observed when 3 is irradiated under...
N₂, and is a commonly observed byproduct in post-irradiated indicating that CO photolysis is another possible photochemical reaction of 3.

Spectroscopic Data for 8: ¹H NMR (300 MHz, C₆D₆): δ 7.85 – 7.71 (m, 6H, P(o-(C₆H₅))₃), 7.41 (d, J = 8 Hz, 1H, py), 6.62 (d, J = 7 Hz, 1H, py), 3.44 (dd, J = 10, 2 Hz, 2H, CH₂P), 2.39 (s, 3H, CH₃), 1.45 (d, J = 13 Hz, 18H, P(C₆H₅)₃), -7.30 (dd, J = 25, 21 Hz, 2H, RuH). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 96.90 (d, J = 212.0 Hz, P(tBu)₂), 58.58 (d, J = 212.7 Hz, PPh₃). FTIR-ATR: (Major stretches) 2009 cm⁻¹, 1962 cm⁻¹, 1891 cm⁻¹, 1872 cm⁻¹.

• Half-life determination of 4.

A J-Young tube was charged with a solution of 3 (9.5 mg, 0.016 mmol) and hexamethylbenzene (0.4 mg, 0.002 mmol) in dry C₆D₆ (0.5 mL) in a N₂-filled glovebox. This solution was used as is (N₂ atmosphere); subjected to three freeze-pump-thaw cycles (static vacuum); or subjected to three freeze-pump-thaw cycles followed by addition of H₂ before being irradiated with a 100 W xenon arc lamp (broad band, no filter) for a period of 1 h at 23 °C. The samples were monitored by ¹H NMR after irradiation to measure the disappearance of 4 and reappearance of 3 by comparing the integrations of the δCH₃ of 4 and 3. All experiments were performed in triplicate and average t₁/₂ is reported (Figs. S21–S24, S29–S30).

Eyring plot of 4 exchange with H₂.

A solution of 10 mg of 3 in ~0.5 mL C₆D₆ was added to a J-Young tube in a N₂ filled glovebox. This tube was sealed and irradiated with a 100 W xenon arc lamp with a 345 nm cutoff filter for 1 h. ¹H NMR spectra were taken from 25 °C to 45 °C in 2.5 °C increments. Line fitting analysis was performed on the -5.14 ppm and -6.10 ppm resonances of 4 and the average width at half height (w₁) of each resonance was determined. The rate constant at each temperature (k₁) was calculated using the following equation:

\[ k₁ = π(w₁ - w₀) \]

Where w₁ is the width at half height of the resonance at a specific temperature and w₀ is the width at half height at 25 °C. An Eyring plot (ln [k₁/T] vs 1/T) was constructed from this data which furnished a straight line with an R² = 0.993 (Figs. S34–S35). This plot furnished a ΔH‡ value of 24.0 ± 1.2 kcal·mol⁻¹ and ΔS‡ value of 22.9 ± 3.4 cal·K⁻¹·mol⁻¹. The ΔG‡ at 293K was calculated to from these values as 17.2 ± 0.17 kcal·mol⁻¹. This experiment was repeated in triplicate.
Figure S1. 300 MHz $^1$H NMR spectrum of 2 in C$_6$D$_6$. 
Figure S2. 121 MHz $^{31}P\{^1H\}$ NMR spectrum of 2 in C$_6$D$_6$. 
**Figure S3.** 75 MHz $^{13}\text{C}^{1\text{H}}$ NMR spectrum of 2 in C$_6$D$_6$. 
Figure S4. $^1\text{H}/^{13}\text{C}$ correlated HSQC spectrum of 2 in $\text{C}_6\text{D}_6$ zoomed in on the aromatic region.
Figure S5. $^1$H/$^{13}$C correlated HSQC spectrum of 2 in C$_6$D$_6$ zoomed in on the aliphatic region.
Figure S6. DOSY spectra of a 50:50 mixture of 1:2 in C₆D₆ zoomed in on the hydride region.
Figure S7. $^1$H-$^1$H ROESY NMR spectrum of 2 in C$_6$D$_6$ zoomed in on the hydride region.
**Figure S8.** Drop-cast FTIR-ATR spectrum of 2.
Figure S9. (top) In-situ 500 MHz $^1$H NMR spectrum of the reaction of 1 with 2 equiv. of KOtBu in THF-$d_8$ at 25°C. The integrated resonances are from 2c. (bottom) In-situ 300 MHz $^1$H NMR of the reaction of 2 with 1 equiv. of KOtBu and 1 equiv. of 18-crown-6 in THF-$d_8$. 

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Figure S10. (top) *In-situ* 202 MHz $^{31}$P{$^1$H} NMR spectrum of the reaction of 1 with 2 equiv. of KOtBu in THF-$_d_8$. (bottom) *In-situ* 121 MHz $^{31}$P{$^1$H} NMR spectrum of a solution of 2 in THF-$_d_8$ treated with 1 equiv. of KOtBu and 1 equiv. of 18-crown-6. The resonance at 99 ppm is unidentified.
Figure S11. 300 MHz $^1$H NMR spectrum of 3 in C$_6$D$_6$. 
**Figure S12.** 121 MHz $^{31}$P$^{1}{H}$ NMR spectrum of 3 in C$_6$D$_6$. 
Figure S13. 101 MHz $^{13}$C{^1}H NMR spectrum of 3 in C₆D₆.
Figure S14. 400 MHz $^1$H-$^1$H ROESY NMR spectrum of 3 in C$_6$D$_6$ zoomed in on the hydride region.
**Figure S15.** Drop-cast FTIR-ATR spectrum of 3.
Figure S16. 300 MHz $^1$H NMR spectrum of the hydride region of complex 3 in C$_7$D$_8$ after heating to 110 °C for 4 h. The resonances at -5.6 ppm and -15.6 ppm are from 3. Trace amounts of complex 2 can be observed at -14.1 ppm. Ru(H)$_2$(CO)(PPh$_3$)$_3$ can also be observed at -6.5 ppm and -8.5 ppm.
Figure S17. 500 MHz $^2$H NMR spectrum of the reaction of 2 with D$_2$ in C$_6$H$_6$ after ~1.5 h under ambient light.
Figure S18. 500 MHz $^1$H NMR spectrum of the reaction of 2 with D$_2$ in C$_6$D$_6$ after ~1 h under ambient light. Zoomed in on the H$_2$ (4.47 ppm) and HD (t, 4.43 ppm) resonances observed (left) and the hydride resonances (right).
Figure S19. 500 MHz $^1$H NMR spectrum of a solution of 2 treated with D$_2$ in C$_6$D$_6$ after 15 min in the dark. Zoomed in on the H$_2$ (4.47 ppm) and HD (t, 4.43 ppm) resonances observed (left) and the hydride resonances (right).
Figure S20. 500 MHz $^2$H NMR spectrum of a solution of 2 treated with D$_2$ in C$_6$H$_6$ spiked with C$_6$D$_6$ after 30 min in the dark.
Figure S21. 300 MHz $^1$H NMR spectra of the $\delta_{\text{CH}_3}$ of 3 and 4 over the course of 2.5 h (bottom to top) after 1 h of broadband irradiation of a solution of 3 in C$_6$D$_6$ at 23 °C under N$_2$(g).
**Figure S22.** Plot of the ln of the peak area of the $\delta_{\text{CH}_3}$ of 4 versus time (s) under N$_2$(g).
Figure S23. 300 MHz $^1$H NMR spectra of the $\delta_{\text{CH}_3}$ of 3 and 4 over the course of 2.5 h (bottom to top) after 1 h of broadband irradiation of a solution of 3 in C$_6$D$_6$ at 23 °C under static-vacuum.
Figure S24. Plot of the ln of the peak area of the $\delta_{\text{CH}_3}$ of 4 versus time (s) under static-vacuum.
Figure S25. 500 MHz $^1$H NMR spectrum of a solution of 3 in C$_6$D$_6$ under H$_2$ after 1 h of broadband irradiation at 23 °C. The integrated resonances are from complex 4.
Figure S26. 121 MHz $^{31}\text{P} \{^{1}\text{H}\}$ NMR of a solution of 3 in C$_6$D$_6$ under H$_2$ after 1 h of broadband irradiation at 23 °C. The labelled peaks are for compound 4. The unlabeled resonances at ~109 ppm and ~60 ppm are from complex 3.
Figure S27. 300 MHz $^1$H-$^1$H ROESY spectrum of a solution of 3 in C₆D₆ under H₂(g) after 1 h of broadband irradiation at 23 °C. (left) Zoomed in on the hydride-hydride exchange correlation, (right) other correlations seen with the hydride resonances. Blue represents through space coupling and red represents exchange coupling.
Figure S28. FTIR-ATR spectrum of a solution of 3 in C₆D₆ under H₂(g) after 1 h of broadband irradiation at 23 °C.
Figure S29. 300 MHz $^1$H NMR spectra of the $\delta_{\text{CH}_3}$ of 3 and 4 over the course of 2.5 h (bottom to top) after 1 h of broadband irradiation of a solution of 3 in $C_6D_6$ at 23 °C under $H_2(g)$.
**Figure S30.** Plot of the ln of the peak area of the $\delta_{\text{CH}_3}$ of 4 versus time (s) under H$_2$(g).
Figure S31. 500 MHz $^1$H NMR spectrum of a solution of 3 in C$_6$D$_6$ under D$_2$ after irradiation with a 345 nm cutoff filter for 1 h at 23 °C. (left) The H$_2$ (4.47 ppm) and HD (t, 4.43 ppm) resonances observed. (middle) Zoomed in on the δ$_{CH_2}$ of 3 and 4. (right) Zoomed in on the hydride region.
**Figure S32.** 500 MHz $^2$H NMR spectrum of a solution of 3 in C$_6$H$_6$ spiked with C$_6$D$_6$ under D$_2$ after irradiation with a 345 nm cutoff filter for 1 h at 23 °C.
Figure S33. 300 MHz $^1$H NMR spectrum of a solution of 3 in C$_6$D$_6$ under D$_2$ after 4 days in the dark. (left) The trace H$_2$ (4.47 ppm) and HD (t, 4.43 ppm) resonances observed. (middle) Zoomed in on the $\delta_{\text{CH}_2}$ of 3. (right) Zoomed in on the hydride region.
**Figure S34.** A VT 500 MHz $^1$H NMR spectra of a solution of 4 in C$_6$D$_6$ under H$_2$(g) (1 atm) at 25–50 °C.
Figure S35. Representative Eyring plot of the rates of exchange obtained from line width analysis of the hydride resonances of 4 under H₂ (1 atm). The barrier (ΔG‡ = 17.2 ± 0.17 kcal·mol⁻¹) was calculated from the slope (ΔH‡ = 24.0 ± 1.2 kcal·mol⁻¹) and x-intercept (ΔS‡ = 22.9 ± 3.4 cal·K⁻¹·mol⁻¹). VT studies were carried out between 25 °C – 50 °C.
Figure S36. 300 MHz $^1$H NMR of a solution of 3 and 10 equiv. PPh$_3$ in C$_6$D$_6$ after 2 h of broadband irradiation at 23 °C zoomed in on the hydride region. Unlabeled peaks are unknown products. (insert) 121 MHz $^{31}$P{$^1$H} NMR of free ligand observed.
Figure S37. 300 MHz $^1$H NMR spectra of a solution of 0.00310 mmol of 3 in C$_6$D$_6$ with 0.155 mmol of ethanol before irradiation (bottom), after 24 h of irradiation with a 345 nm cutoff filter (middle), and after spiking the sample with 1 µL of ethyl acetate.
Figure S38. 300 MHz $^1$H NMR spectra of a solution of 0.00310 mmol of 3 in C$_6$D$_6$ with 0.0931 mmol of 1-phenylethanol before irradiation (bottom), after 7 h of irradiation with a 345 nm cutoff filter (middle), and after spiking the sample with 1 µL of acetophenone.
Figure S39. 300 MHz $^1$H NMR spectra of a solution of 0.00480 mmol of 3 in C$_6$D$_6$ with 0.0970 mmol of 2-propanol before irradiation (bottom), after 18 h of irradiation with a 345 nm cutoff filter (middle), and after spiking the sample with 1 µL of acetone.
Figure S40. 500 MHz $^1$H NMR spectra of the hydride region of a solution of 0.0030 mmol of 3 in CD$_3$OD before irradiation (bottom) and after 6 h of irradiation with a 345 nm cutoff filter (top).
Figure S41. QE-GCMSMS headspace mass spectrum (above) and chromatogram (below) of an aliquot (10 µL) of a solution of 3 in methanol after 5 h of irradiation with a 345 nm cutoff filter at 23 °C. A broad peak at 1.50 minutes corresponded to a mass of 30.0101 amu which is in agreement to the formula CH₂O (M$_{calc'd}$ = 30.0106) with a 1.46 ppm error.
Figure S42. Direct injection (10 µL) of an aliquot of a solution of 3 in methanol after 5 h of irradiation with a 345 nm cutoff filter at 23 °C, exposed to ambient atmosphere, into a QE-LCMSMS (above) showed a peak consistent with the formula, [Ru(H)(LutP)(CO)]⁺ ([M⁺]calc’d = 382.0868; [M⁺]found = 382.0862) and consistent with calculated isotopic distribution (below). A second peak consistent with carbonylation was observed ([M+CO]calc’d = 410.0817 ;[M+CO]found = 410.0811). In addition, peaks with masses consistent with oxidized LutP and triphenylphosphine were observed in the mass spectrum.
Figure S43. 300 MHz $^1$H NMR spectra of a solution of 0.046 mmol of 3 in C$_6$D$_6$ and 0.057 mmol of paraformaldehyde before irradiation (bottom), after 4 h of irradiation with a 345 nm cutoff filter (middle), and after 6 h of irradiation with a 345 nm cutoff filter and left overnight in ambient light (top).
Figure S44. (top) 500 MHz $^1$H NMR spectrum of a solution of 3 in C$_6$D$_6$ and 2-propanol-$d_8$. (bottom) The same solution after 1.5 h of broadband irradiation at 23 °C. (left) Zoomed in on the H$_2$, HD, and $\delta$CH$_2$ regions. (right) Zoomed in on the hydride region.
Figure S45. 500 MHz $^2$H NMR spectrum of a solution of 3 in C$_6$H$_6$ (spiked with C$_6$D$_6$) and 2-propanol-$d_8$ after 1.5 h of broadband irradiation at 23 °C.
**Figure S46.** GC trace (zoomed in on the H\textsubscript{2} region) of the headspace samplings of a solution of 3 in 2-propanol after 1 h of irradiation at 23 °C with a 345 nm (black), 420 (blue), or 515 nm (green) cutoff filter.
Figure S47. 300 MHz $^1$H NMR of a solution of 3 in C$_6$D$_6$ before irradiation (bottom) and after 1 min of irradiation at 23 °C with a 515 nm cutoff, 420 nm cutoff, 345 nm cutoff, and UV band pass filter.
Figure S48. 300 MHz $^1$H NMR spectrum of a solution of 3 and ethanol in C$_6$D$_6$ after 4.5 h of irradiation with a 345 nm cutoff filter zoomed in on the hydride region. The same species were observed for 2-propanol and 1-phenylethanol; note for methanol, these species were not observed and 8 was the major species.
Figure S49. 300 MHz $^1$H NMR spectrum of a solution of 3 under an atmosphere of N$_2$(g) (bottom), and CO(g) (top) in C$_6$D$_6$ after 1 h of broadband irradiation (e.g., solution containing 8).
Figure S50. 121 MHz $^{31}$P NMR spectrum of a solution of 3 under an atmosphere of N$_2$ (bottom), and CO (top) in C$_6$D$_6$ after 1 h of broadband irradiation (e.g., solution containing 8).
Figure S51. Drop-cast FTIR-ATR spectrum of 3 under CO$_2$ gas after 1 h of broadband irradiation (spectrum of solution containing 8).
Figure S52. Overlayed UV-vis spectra of complex 0.182 mM 2 (red) and 0.25 mM 3 (black). Beer’s law plots were obtained for complexes 2 and 3. Molar absorptivity of 2 at 410 nm is 770 M⁻¹·cm⁻¹. Molar absorptivity of 3 at 320 nm is 4,800 M⁻¹·cm⁻¹.
Table S1. Crystal data and structure refinements for 2 and 3.

| Complex |  | 2 | 3 |
|---------|---|---|---|
| Identification code | rlacy87_abs | rlacy86_abs |
| Empirical Formula | C$_{34}$H$_{41}$NOP$_2$Ru | C$_{40}$H$_{49}$NOP$_2$Ru |
| Formula weight | 642.69 | 722.81 |
| Temperature | 104(7) K | 100.0(4) K |
| Wavelength | 1.54184 Å | 0.71073 Å |
| Crystal system | Triclinic | Triclinic |
| Space group | P -1 | P -1 |
| Unit cell dimensions | a = 9.2220(2) Å, b = 11.9881(3) Å, c = 15.2279(3) Å | a = 10.67863(16) Å, b = 13.6063(2) Å, c = 14.2941(2) Å |
| Volume | 1559.37(6) Å$^3$ | 1817.97(5) Å$^3$ |
| Z | 2 | 2 |
| Density (calculated) | 1.369 Mg/m$^3$ | 1.320 Mg/m$^3$ |
| Absorption coefficient | 5.235 mm$^{-1}$ | 0.550 mm$^{-1}$ |
| F(000) | 668 | 756 |
| Crystal size | 0.251 x 0.043 x 0.018 mm$^3$ | 0.202 x 0.15 x 0.111 mm$^3$ |
| Theta range for data collection | 3.016 to 77.088° | 2.864 to 27.101° |
| Index ranges | -9<=$h<=$11, -15<=$k<=$15, -19<=$l<=$19 | -13<=$h<=$13, -16<=$k<=$17, -18<=$l<=$18 |
| Reflections collected | 33481 | 40381 |
| Independent reflections | 6554 [R(int) = 0.0585] | 8026 [R(int) = 0.0411] |
| Completeness to theta | 99.9% (theta = 67.684°) | 99.9% (theta = 25.242°) |
| Absorption correction | Gaussian | Gaussian |
| Max. and min. transmission | 1.000 and 0.519 | 1.000 and 0.485 |
| Refinement method | Full-matrix least-square on F$^2$ | Full-matrix least-square on F$^2$ |
| Data / restraints / parameters | 6554 / 0 / 362 | 8026 / 0 / 419 |
| GooF on F$^2$ | 1.076 | 1.054 |
| Final R indices [I>2sigma(I)] | R1 = 0.0348, wR2 = 0.0918 | R1 = 0.0245, wR2 = 0.0604 |
| R indices (all data) | R1 = 0.0373, wR2 = 0.0935 | R1 = 0.0309, wR2 = 0.0630 |
| Extinction coefficient | n/a | n/a |
| Largest diff. peak and hole | 0.891 and -1.347 e.Å$^{-3}$ | 0.555 and -0.551 e.Å$^{-3}$ |
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