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Inner- and Outer-Sphere Roles of Ruthenium Phosphido Complexes in the Hydrophosphination of Alkenes

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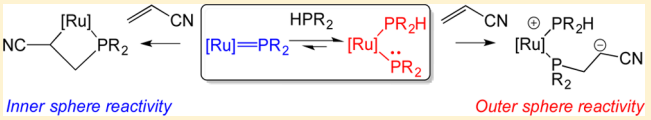
Supporting Information

ABSTRACT: An inner-sphere synthetic cycle for the hydrophosphination of alkenes is proposed, based on observed [2 + 2] cycloaddition of a wide range of alkenes at a coordinatively unsaturated Ru═PR_2 complex. Key intermediates in the cycle were prepared, and their reactions with various organic acid/base pairs were examined to identify both new ruthenium precursors and base cocatalysts that allow turnover of the proposed cycle. Two new cationic ruthenium indenyl phosphine complexes were isolated and structurally characterized. Although preliminary screening studies show the moderate activity of these and related neutral phosphido complexes for catalytic hydrophosphination of acrylonitrile by both $HPPh_2$ and $HPCy_2$, and comparable activity for the hydrophosphination of *tert*-butyl acrylate by $HPPh_2$, no activity was observed for the analogous hydrophosphination of 1-hexene. This is attributed to strong binding of the substrate phosphine to the unsaturated, planar Ru═PR_2 fragment generated in situ, which inhibits the inner-sphere, alkene cycloaddition mechanism. An alternative, outer-sphere Michael addition process, involving a saturated complex with a strongly nucleophilic pyramidal Ru−PR_2 ligand, is proposed to rationalize the observed selectivity for catalytic hydrophosphination of activated, but not simple, alkenes. Implications for further catalyst development are discussed.



INTRODUCTION

The hydrophosphination of alkenes by primary or secondary phosphines represents an atom-economical route to the synthesis of secondary or tertiary phosphines containing new alkyl substituents. Unlike the analogous N−H addition reaction, hydroamination, a catalyst is not necessarily required for hydrophosphination: the reaction can occur thermally or photochemically or can be initiated by acids, bases, or radicals.[1] However, *catalytic* hydrophosphination can potentially introduce regio- and stereoselectivity into this process that may obviate the tedious and reagent-wasting separations currently required in the production of structurally sophisticated and value-added phosphine ligands. Catalytic hydrophosphination may also allow the introduction of P-alkyl groups that are challenging to obtain via noncatalyzed hydrophosphination processes or classic, stoichiometric salt metathesis routes employing MPR_2 or $ClPR_2$ reagents.

Accordingly, interest in metal-catalyzed hydrophosphination has been growing,[2] and among recent examples, the importance of metal phosphido (M−PR_2) intermediates has been increasingly highlighted. In early, or electron-deficient, metal systems the insertion of alkenes into the M−P bond appears to be critical to P−C bond formation,[3] while for many examples of late, or electron-rich, metal centers, the substrate scope seems to indicate the importance of a Michael-type addition of the highly nucleophilic phosphido P at activated, electrophilic alkenes.[4] Thus, an apparent dichotomy exists between catalytic systems participating in inner-sphere, versus outer-sphere, P−C bond-forming reactions.

We previously described the synthesis of a series of highly reactive terminal phosphido complexes Ru(η^5-indenyl)(═PR_2)(PPh_3) (**1**), which are prepared via dehydrohalogenation of the corresponding secondary phosphine complexes Ru(η^5-indenyl)Cl(PR_2H)(PPh_3) (**2**) using the strong base KOBu^t.[5] We have investigated particularly thoroughly the reactions of **1** for R = Cy, which include the intriguing [2 + 2] cycloaddition of a range of both simple *and* activated alkenes, giving metallacycles **3**.[6] The mechanism by which this P−C bond-forming reaction occurs is of particular interest, given the wide scope of alkenes that can participate, and the limited examples in the literature of such well-defined insertions of alkenes into metal−heteroatom bonds. A manuscript describing our kinetic and computational investigation of this process is currently in preparation.[7] However, the cycloaddition of alkenes at this Ru═P double bond also represents the basis of a synthetic, potentially catalytic, cycle leading to hydrophosphination (Figure 1). The cycle features the use of an external base to deprotonate the metal-coordinated secondary phosphine, similar to some mechanisms that have been proposed for late-metal-catalyzed hydrophosphination.[8,9] The resulting conjugate acid can then deliver the proton to complete the hydrophosphination cycle: in this case it is essential for protonolysis of the metallacycle formed from the apparent inner-sphere cycloaddition step.

We present here reactions of complexes **1** and **2** confirming the viability of this synthetic cycle, including studies to identify

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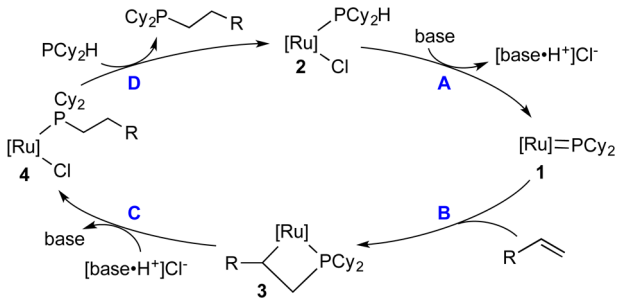
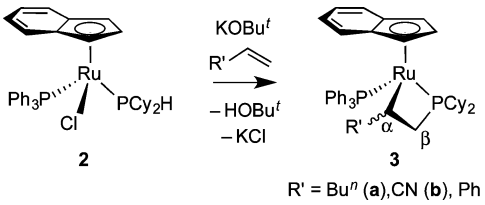


Figure 1. Synthetic cycle for the inner-sphere hydrophosphination of alkenes by the secondary phosphine $HPCy_2$, mediated by coordinatively unsaturated phosphido complex **1** ([Ru] = Ru(η^5-indenyl)PPh_3).

a base capable of acting as a "proton shuttle" as shown in Figure 1. We report also our preliminary assessment of a series of related Ru indenyl complexes for their activity as catalyst precursors for alkene hydrophosphination. This points to the operation of an alternative, outer-sphere cycle for hydrophosphination under catalytic conditions and provides insight into the challenges of developing late-metal catalysts for the hydrophosphination of unactivated alkenes.

RESULTS AND DISCUSSION

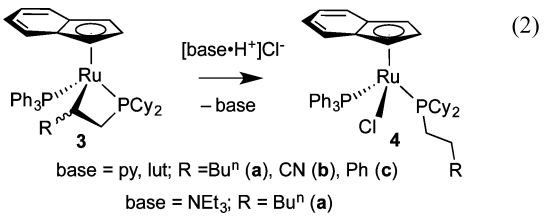
Identifying a Proton Shuttle. To identify the optimal base cocatalyst for hydrophosphination using this ruthenium indenyl system, we first screened various organic acids for their ability to effect protonolysis of metallacycles **3** (step **C** in Figure 1). Although we previously generated a series of metallacycles from the addition of alkenes to isolated samples of complex **1**,[6] for these reactivity studies we implemented a "one-pot" procedure to obtain the metallacycles directly from the secondary phosphine precursor complex **2** (eq 1). The addition of excess



(1)

alkene to **2** in toluene in the presence of $KOBu^t$ allows the formation of **1** in situ at room temperature and its subsequent reaction to form metallacycle products. This is a cleaner and higher-yielding alternative to isolating the highly soluble and very reactive **1**. We prepared both of the previously characterized metallacycles **3a,b**, where R = Cy and R′ = Bu^n, CN, respectively, and a new analogue **3c** derived from styrene (R′ = Ph) using this method. The cleanliness of this one-pot procedure bodes well for the ultimate adaptation of this chemistry to catalysis: the presence of excess unsaturated reagent as required in step **B** in Figure 1 does not interfere with the base-mediated phosphine deprotonation in step **A**.

Possible protonolysis reactions of the three representative metallacycles **3a–c** were monitored by $^{31}P\{^1H\}$ NMR. These experiments indicated that neither the secondary phosphine substrate $HPCy_2$ (pK_a = 35.7 (THF)[10]) nor Bu^tOH (pK_a = 19.2 (H_2O)[11]), the conjugate acid of the base we use to prepare **1**, is sufficiently acidic to effect such protonolysis at the isolated metallacycles. However, stronger acids such as pyridine and lutidine hydrochlorides (pK_a = 5.25 and 6.70 (H_2O), respectively[12]) will cleave the Ru–C bond in all three metallacycles, to give the new mixed phosphine products Ru(η^5-indenyl)Cl{$PCy_2(CH_2CH_2R')$}PPh_3 (**4a–c**) (eq 2).



(2)

The identity of **4a** (R′ = Bu^n), isolated from a larger-scale reaction of **3a** with pyridine hydrochloride, was confirmed by LIFDI-MS analysis (see the Supporting Information). $^{31}P\{^1H\}$ NMR analysis of a d_6-benzene sample of **4a** showed that ligand redistribution occurs readily in solution: singlets due to the symmetric bis(phosphine) complexes Ru(η^5-indenyl)Cl$(PPh_3)_2$ and (presumably) Ru(η^5-indenyl)Cl{$PCy_2(CH_2CH_2Bu^n)\}_2$ slowly replaced signals for **4a** over 24 h. Further ligand substitution reactions occurred with the addition of excess $HPCy_2$ to a solution of **4a** generated in situ from the addition of pyridine hydrochloride; the product mixture included the regenerated mixed phosphine complex Ru(η^5-indenyl)Cl-$(PCy_2H)(PPh_3)$ (**2**). These observations are an encouraging indication of the substitutional lability of the product phosphine, which is critical to a putative catalytic cycle in the presence of excess $HPCy_2$ (step **D**, Figure 1). The weakest acid able to participate in the protonolysis, observed only for **3a**, is triethylamine hydrochloride (pK_a = 10.7 (H_2O)[13]). However, neither pyridine nor triethylamine, conjugate bases of sufficiently acidic salts, are capable of dehydrohalogenating the secondary phosphine precursor **2** (step **A** in Figure 1), as determined by $^{31}P\{^1H\}$ NMR; only signals due to unreacted **2** were observed.

These results suggested that starting from halide-free, cationic analogues of complex **2** would simplify the role of the added base in a putative catalytic cycle (Figure 2). This

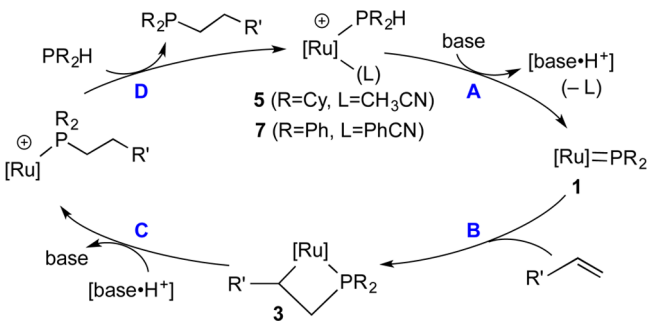


Figure 2. Possible catalytic cycle for the inner-sphere hydrophosphination of alkenes, in which phosphido complex **1** forms from halide-free, cationic precursors ([Ru] = Ru(η^5-indenyl)PPh_3) that contain labile nitrile ligands L.

would also prevent competition of the Cl^- ligand with the alkene and secondary phosphine substrates for coordination at Ru. Furthermore, cationic secondary phosphine complexes should exhibit P–H bond acidity higher than that of their neutral chloride analogues,[14] which might allow the use of weaker bases as cocatalysts (providing stronger conjugate acids for the eventual protonolysis step). We assessed the possible participation of the cationic complex [Ru(η^5-indenyl)(NCMe)-

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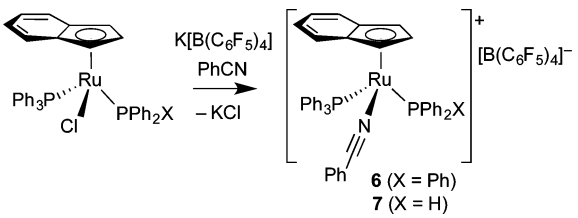
$(PCy_2H)(PPh_3)_2][PF_6]$ (**5**) in the revised synthetic cycle shown in Figure 2. Previous studies indicated the high lability of the acetonitrile ligand in **5** and also the ready in situ generation of **1** from this complex in the presence of the strong base $KOBu^t$.[5b] However, **5** did not react with NEt_3 to generate complex **1** (step **A** in Figure 2), as determined by $^{31}P\{^1H\}$ NMR. The cation did react with the stronger base 1,8-diazabicycloundec-7-ene (DBU; pK_a of the conjugate acid 13.5 (H_2O)[15]) to give **1** in situ; addition of acrylonitrile "trapped" the reactive phosphido complex as the metallacycle **3b**.

The above results demonstrate the viability of the synthetic hydrophosphination cycle shown in Figure 2 for R = Cy, although we have not yet identified conditions/reagents to allow a full cycle in a one-pot reaction.[16] At this point we decided to switch our focus to the use of the more acidic phosphine $HPPh_2$. This secondary phosphine is by far the most commonly used substrate for catalytic hydrophosphination, perhaps because of its ready availability, but probably also because of its relatively low pK_a.[17] The greater acidity of this phosphine, relative to $HPCy_2$, should encourage a larger equilibrium constant for deprotonation by DBU, an intermediate-strength base, in step **A** of the cycle shown in Figure 2, providing higher concentrations of both the phosphido complex **1** (with R = Ph) and the conjugate acid DBU·H^+. Thus, as described below, we screened a series of halide-free ruthenium indenyl complexes for their activity in hydrophosphination reactions of $HPPh_2$.

Catalyst Precursor Complexes. We prepared the two new cationic complexes $[Ru(\eta^5\text{-indenyl})(NCPh)(PPh_3)_2][B(C_6F_5)_4]$ (**6**) and $[Ru(\eta^5\text{-indenyl})(NCPh)(PPh_2H)(PPh_3)][B(C_6F_5)_4]$ (**7**) through the addition of $K[B(C_6F_5)_4]$ to the corresponding neutral chloride precursors (eq 3). These



(3)

complexes both contain the labile benzonitrile ligand, which addresses a possible interference in the putative catalytic cycle of competing metalation of an acetonitrile ligand by the highly basic phosphido ligand in **1**.[5b] The $[B(C_6F_5)_4]^-$ counterion helps to ensure the higher solubility of these ionic complexes in less polar solvents such as benzene. We presumed that facile substitution of one or more ligands at **6** would occur in the presence of excess $HPPh_2$, allowing the entry of this complex into the putative catalytic cycle shown in Figure 2 prior to step **A**.

The solution structures of complexes **6** and **7** were confirmed by ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR spectroscopy and ESI mass spectrometry (see the Experimental Section and the Supporting Information). IR spectroscopy (KBr) also confirmed the presence of the benzonitrile ligands in these complexes, showing ν_{CN} 2228 and 2237 cm^{-1} for **6** and **7**, respectively.[18] Single crystals suitable for X-ray diffraction analysis were also obtained for both complexes: the solid-state molecular structures are shown in Figure 3, and selected interatomic distances and bond angles are shown in Table 1. Crystallographic indenyl slip factors (Δ) of 0.16 and 0.11 Å for **6** and **7**, respectively, are well within the normal range for η^5 coordination of the indenyl ring in these pseudo-octahedral

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for the Molecular Structures of the Cations from $[Ru(\eta^5\text{-indenyl})(NCPh)(PPh_3)_2][B(C_6F_5)_4]\cdot 2.5C_6H_6$ (6) and $[Ru(\eta^5\text{-indenyl})(NCPh)(PPh_2H)(PPh_3)][B(C_6F_5)_4]$ (7)[a]

	6	7
Ru–P1	2.3123(5)	2.3148(5)
Ru–P2	2.3664(5)	2.2889(5)
Ru–N	2.0426(16)	2.0310(16)
Ru–C*	1.904	1.893
Ru–H1P		1.34(2)
Δ	0.16	0.11
P1–Ru–P2	98.240(17)	92.932(19)
P1–Ru–N	96.82(5)	91.07(5)
P2–Ru–N	91.84(5)	89.61(5)
Ru–P1–H1P		117.4(9)
Ru–N–C10	169.95(16)	178.66(17)
P1–Ru–C*	120.4	124.4
P2–Ru–C*	121.2	124.1
N–Ru–C*	121.9	124.8

[a]C* denotes the centroid of the plane defined by C(7A)–C(1)–C(2)–C(3)–C(3A), and Δ is the "indenyl crystallographic slip distortion", defined as d(Ru–C(7A),C(3A)) − d(Ru–C(1),C(3)).[19]

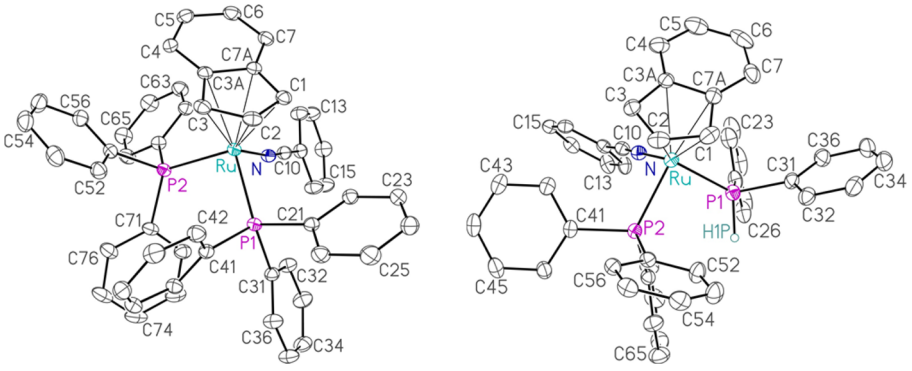


Figure 3. Molecular structures of the cations from $[Ru(\eta^5\text{-indenyl})(NCPh)(PPh_3)_2][B(C_6F_5)_4]\cdot 2.5C_6H_6$ (**6**; left) and $[Ru(\eta^5\text{-indenyl})(NCPh)(PPh_2H)(PPh_3)][B(C_6F_5)_4]$ (**7**; right). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. The hydrogen atom attached to P1 in complex **7** is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown.

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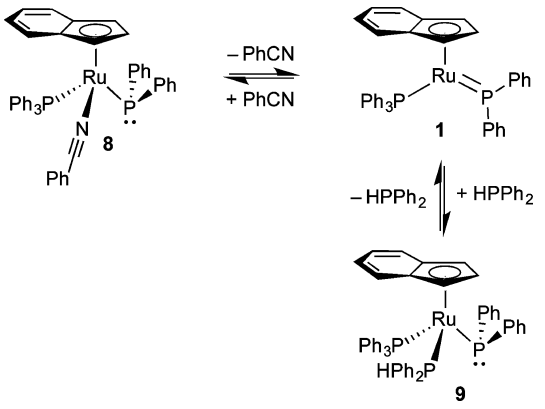
complexes;[19] the slightly larger value for complex **6** is consistent with more steric crowding in this bis(triphenylphosphine) complex, although this value is still much smaller than the corresponding slip factor of 0.21 Å reported for the crystal structure of its neutral chloride-containing precursor.[20] The greater steric crowding in **6**, relative to **7**, can also be seen from the wider angles at Ru between the two phosphine and nitrile donor atoms and a slight loss of linearity in the Ru−nitrile linkage: the Ru−N−C10 bond angle in **6** is 169.95(16)°, while the nitrile in **7** is almost linear, with an analogous angle of 178.66(17)°.

The cationic complexes **6** and **7** both provide entry points prior to step **A** in the putative cycle shown in Figure 2. We also chose to investigate the catalytic activity of two neutral, halide-free complexes containing the terminal PPh_2 ligand, whose structures are related to the coordinatively unsaturated complex **1** by simple equilibria (Scheme 1); these give an entry point

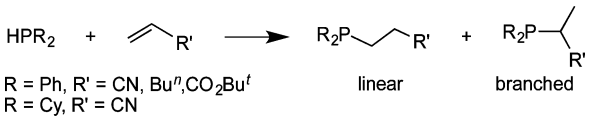
Scheme 1



prior to step **B** in the catalytic cycle in Figure 2. We previously reported the dark purple-red benzonitrile complex Ru(η^5-indenyl)(PPh_2)(NCPh)(PPh_3) (**8**), which behaves as a masked source of the Ru=PPh_2 moiety;[21] the thermal decomposition of **8** to the ortho-metalated complex Ru(η^5-indenyl){κ^2-(*o*-C_6H_4)PPh_2}(PPh_2H) provides strong evidence for the facile dissociation of benzonitrile to give **1** (R = Ph) in situ, and this was further supported by reactions with hydrogen and 1-hexene, which gave 1,2-addition and [2 + 2] cycloaddition products, respectively, analogous to those observed for reactions of the same substrates with **1** (R = Cy, Pr^i).[5] The facile loss of benzonitrile from **8** allows this precursor to enter the synthetic cycle at step **B** (Figure 2). The benzonitrile ligand in **8** is readily substituted by 1 equiv of secondary phosphine to give the deep purple mixed phosphine/phosphido complex Ru(η^5-indenyl)(PPh_2)(PPh_2H)(PPh_3) (**9**), which is also related to **1** by a simple equilibrium (±PPh_2H; Scheme 1).[22] We have isolated complex **9** and included it in the catalyst screening reactions described below.

Catalysis. We screened the activity of complexes **6**−**9** for hydrophosphination of the activated substrate acrylonitrile by Ph_2PH (entries 1−4, Table 2), in the presence of the base cocatalyst DBU, in NMR-tube reactions monitored by $^{31}P\{^1H\}$ NMR. All four complexes showed moderate activity at room temperature and 10% catalyst loading, giving conversions of 72−92% over 24 h to the linear, anti-Markovnikov product $Ph_2PCH_2CH_2CN$ and small amounts (≤13%) of the branched product $Ph_2PCH(CN)CH_3$. A control reaction (entry 5) with no added Ru precatalyst or base cocatalyst indicated a thermal

Table 2. Reactions Screening the Activity of Complexes 6−9 in Catalytic Hydrophosphination[a]



entry	complex	Ru:DBU (mol %)	early TOF (h^{-1})[b]	overall conversion (%)[c]	linear:branched
$HPPh_2$ + H_2C=CH(CN):					
1	**6**	10:10	2(0.6)	76(1)	94:6
2	**7**	10:10	0.9(0.1)	90(4)	98:2
3	**8**	10:10	7(0.6)	92(6)	87:13
4	**9**	10:10	2 (0.5)	72(5)	92:8
5		0:0		8(2)[d]	99:trace
6		0:10	0.4(0.2)	41(10)	89:11
7	**8**	5:5	13(1)	73(10)	87:13
8	**6**	10:0		7(3)	99:trace
9	**7**	10:0		1(0)	99:trace
10	**8**	10:0	5(0)	74(1)	75:25
11	**9**	10:0	2(0.6)	66(3)	90:10
$HPPh_2$ + H_2C=CH(Bu^n)					
12	**8**	10:10		trace[d]	
13	**8**	10:0		trace	
$HPPh_2$ + H_2C=CH(CO_2Bu^t)					
14	**8**	10:0	2.9(0.2)	74(3)	99:trace
15	**9**	10:0	1.7(0.3)	75(4)	99:trace
16		0:0		8[e]	99:trace
17		0:10		36[e]	99:trace
$HPCy_2$ + H_2C=CH(CN)					
18	**6**	10:10	0.7 (0.1)	43(12)[d]	99:trace
19		0:0		trace	
20		0:10		trace	

[a]Reactions were carried out in 3/1 THF/d_6-benzene in NMR tubes at room temperature, with periodic shaking to ensure mixing. For each entry, alkene and secondary phosphine were present in equimolar concentrations, and the results shown are the average of triplicate runs. [b]Quantitative $^{31}P\{^1H\}$ NMR experiments (128 scans, relaxation delay 55 s) were initiated within 15 min of sample preparation. These experiments required 2 h 44 s, so the resulting spectra provide time-averaged signal intensities corresponding approximately to the first 1 h of reaction time. Unless otherwise noted, maximum deviations from the average for triplicate runs are shown in parentheses. [c]Unless otherwise noted, conversions were calculated for spectra obtained after 24 h, from relative integration of ^{31}P signals for hydrophosphination product isomers[26] and free HPR_2. Other signals appeared in the region due to Ru−P-containing complexes. This formula necessarily underestimates the conversions obtained for catalysts **7**−**9**, all of which contain 1 equiv or more of "PPh_2" that may be incorporated in one or more of the products or residual $HPPh_2$. Maximum deviations from the average for triplicate runs are shown in parentheses. [d]Conversion calculated for 48 h of reaction, instead of 24 h. [e]Results from just one experiment.

background reaction giving less than 10% conversion to almost exclusively the linear regiosiomer over the same time period, as previously observed by Glueck[23] and Morris[14] for the same reaction catalyzed by Pt and Ru, respectively.[24] Complicating interpretation of these results is our observation that this hydrophosphination reaction is also catalyzed by DBU itself under these conditions: entry 6 in Table 2 shows that, in the absence of Ru, 10 mol % DBU gives 41% conversion, with regioselectivity similar to that observed for the Ru/base cocatalyst mixtures. This was not entirely unanticipated; the

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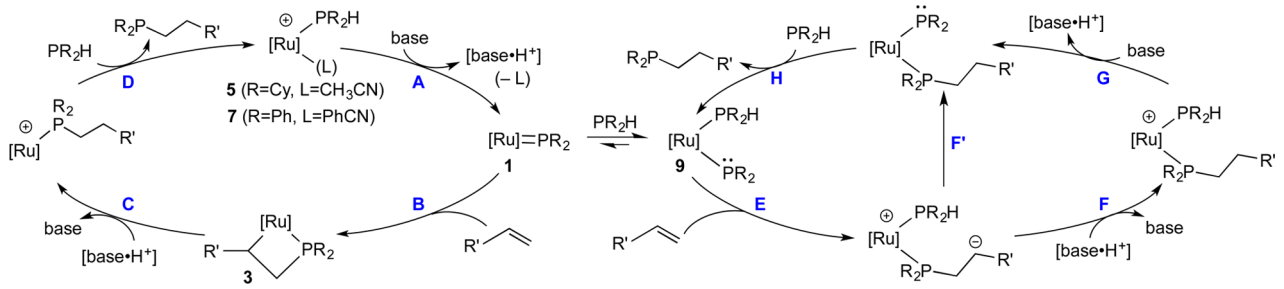

Figure 4. Inner- and outer-sphere catalytic cycles for the hydrophosphination of alkenes ([Ru] = Ru(η^5-indenyl)PPh_3). The two cycles are linked by the equilibrium between intermediate **1** and its $HPPh_2$ adduct, complex **9**, which apparently competes effectively with cycloaddition of alkene substrates at **1**.

use of 1 mol % $KOBu^t$ in this reaction under similar conditions (THF, room temperature) was recently reported to give "less than 10%" conversion after 24 h,[14] which works out to approximately the same overall activity we are observing for DBU.[25]

We calculated "initial" turnover frequencies (TOF) to gauge the progress of these reactions after approximately 1 h (Table 2), to get a sense of how efficiently each of the catalyst precursors was being activated for catalysis. Since we obtained both the highest initial TOF and the highest overall conversion for the neutral phosphido complex **8** (entry 3), we also assessed the activity of this complex for a lower catalyst loading of 5 mol % (entry 7, Table 2), finding a higher initial TOF and only slightly reduced conversion over 24 h. However, despite the relatively high catalytic activity of complex **8** for the hydrophosphination of acrylonitrile by $HPPh_2$, this phosphido complex shows essentially no activity for the hydrophosphination of 1-hexene under comparable conditions (Table 2, entry 12), even after 48 h. If we assume that the catalytic cycle shown in Figure 2 is in effect for the acrylonitrile reaction, the absence of catalysis for 1-hexene could be ascribed to a much lower rate of cycloaddition of 1-hexene, relative to acrylonitrile. For example, kinetic studies of alkene cycloadditions at the Ru=PCy_2 analogue of **1** show that the rate constant for cycloaddition of 1-hexene is at least 2 orders of magnitude smaller than that for cycloaddition of acrylonitrile.[7] Such a rate difference might be sufficient to allow other reactions of the Ru precatalyst to compete effectively with productive catalysis.

Another possible explanation for the lack of activity of complex **8** in the hydrophosphination of 1-hexene by $HPPh_2$ is that the cycle shown in Figure 2 is not accessible for either alkene substrate, under catalytic conditions. Although we know from previous studies that benzonitrile dissociation occurs readily from complex **8** to generate the coordinatively unsaturated "Ru=PPh_2" in solution,[21] in the presence of excess $HPPh_2$ complex **8** reacts rapidly to give the secondary phosphine/phosphido complex **9**.[27] Figure 4 illustrates how this complex represents an entry point into an alternative catalytic cycle that relies on the outer-sphere Michael addition of the pyramidal phosphido ligand in this coordinatively saturated complex at the electron-deficient, activated acrylonitrile substrate.[28] Such nucleophilic addition would be unlikely to occur at the electron-rich 1-hexene. Tellingly, the only signals observed in the Ru–P region of $^{31}P\{^1H\}$ NMR spectra for the reactions of 1-hexene with $HPPh_2$ in the presence of complex **8** (Table 2, entries 12 and 13) are those due to complex **9**, whereas for the reactions of acrylonitrile with $HPPh_2$ mediated by either **8** or **9** (Table 2, entries 3, 4, 7, 10, and 11) we do not see complex **9** but do see a variety of Ru-containing species whose signals are attributable to mixed phosphine and mixed phosphine/phosphido complexes of varying composition.[29] Further support for the relevance of this outer-sphere catalytic cycle comes from the fact that we do not observe signals due to the putative metallacycle intermediate **3** that would form from cycloaddition of acrylonitrile or 1-hexene in spectra of the reaction mixtures represented by entries 3, 4, and 12 in Table 2,[30] although this does not rule out the possibility that such intermediates are forming and are rapidly consumed in subsequent protonolysis reactions. We previously showed that this metallacycle is formed in the reaction of **8** with 1-hexene in d_6-benzene[31] but that the analogous carbonyl adduct Ru(η^5-indenyl)(PPh_2)(CO)(PPh_3), which forms irreversibly and is *not* a source of the Ru=PPh_2 fragment, does not react with this simple alkene.[32] Thus, the fact that we observe no signals for metallacycle formation *and* that we observe no catalytic turnover for 1-hexene suggests that the formation of **9** from **8** under our catalyst screening conditions may be similarly irreversible: in other words, if the equilibria shown in Scheme 1 lie heavily toward complex **9**, complex **8** cannot be regarded as a source of "Ru=PPh_2" in the presence of excess $HPPh_2$. A thermolysis experiment monitoring the decomposition of complex **9** to the ortho-metalated complex Ru(η^5-indenyl)-{κ^2-(*o*-C_6H_4)PPh_2}(PPh_2H) via dissociation of $HPPh_2$ suggests that the barrier to this dissociation is higher than that for the corresponding dissociation of benzonitrile from complex **8**; the half-life for decomposition of complex **9** at 60 °C is about 96 h, in comparison to 4 h for complex **8**.[21] It is likely that, in the presence of excess $HPPh_2$, loss of $HPPh_2$ from complex **9** to regenerate the vacant coordination site at **1** is not sufficiently favored to allow competitive alkene cycloaddition.

The outer-sphere catalytic cycle shown on the right side of Figure 4 includes a zwitterionic intermediate that results from nucleophilic attack of the phosphido ligand in complex **9** at the electrophilic carbon of the acrylonitrile double bond in step **E**. We had presumed, on the basis of the inner-sphere cycle proposed in Figure 2, that external base would act as a proton shuttle in these reactions; $[DBU{\cdot}H]^+$ present in the reaction mixture would be required to protonolyze the proposed metallacyclic intermediate. In the outer-sphere cycle in Figure 4, the role of this proton source is simply to "quench" the carbanion in the zwitterionic intermediate (step **F**); the base is then available to deprotonate another 1 equiv of Ru-bound secondary phosphine (step **G**). However, this carbanion is likely to be extremely basic[14] and thus could be protonated by species far less acidic than $[DBU{\cdot}H]^+$. For example, Glueck has shown that either Pt–H or added Bu^tOH or water can transfer a proton to a similar carbanion during Pt-catalyzed hydrophosphination,[4a,b] while Morris has proposed that even free

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$HPPh_2$ can play this role in the hydrophosphination of acrylonitrile catalyzed by a Cp*Ru phosphido complex, generating free $[PPh_2]^-$, which competes for binding to Ru in the reaction mixture.[14] Consistent with this hypothesis, we find that both phosphido complexes **8** and **9** are active for the hydrophosphination of acrylonitrile in the absence of DBU cocatalyst (entries 10 and 11 in Table 2).[33] As for the Morris system, the most likely proton source in these mixtures is the substrate $HPPh_2$; we have not yet undertaken experiments to determine whether the protonation step is intermolecular (i.e., from free phosphine in the mixture) or intramolecular (from a more acidic Ru-bound $HPPh_2$). The intramolecular pathway (**F′** in Figure 4) is an appealing one, though, since it directly generates not only the product tertiary phosphine, which can undergo substitution by incoming $HPPh_2$, but also a new PPh_2 phosphido ligand, capable of intermolecular nucleophilic attack at acrylonitrile.

Although the proposed outer-sphere hydrophosphination mechanism shown in Figure 4 is consistent with the observed reactivity of activated acrylonitrile versus unactivated 1-hexene, an alternative outer-sphere mechanism involving the intermolecular attack of free $HPPh_2$ at a putative N-bound acrylonitrile−ruthenium adduct would also account for this substrate selectivity.[34] Precedent for this mechanism comes from Togni's studies of the Ni-catalyzed enantioselective hydrophosphination of methacrylonitrile by a range of secondary phosphines.[35] However, unlike the Togni system, formation of the acrylonitrile adduct in our system does not seem to be favored. In screening reactions of the four catalyst precursors examined in this study, we found evidence for the formation of such an adduct only for complex **6**: a new ^{31}P singlet at 46.9 ppm, consistent with the formula $[Ru(\eta^5\text{-indenyl})(NCCH{=}CH_2)(PPh_3)_2]^+$, appears adjacent to the signal due to unreacted **6**, when excess acrylonitrile is added to **6** in the absence of $HPPh_2$ (Figure S21 in the Supporting Information). The same signal appears only transiently, and at much lower intensity, when both excess acrylonitrile and excess $HPPh_2$ are added to **6**. This signal does not show up at all under catalytic conditions, when DBU is also present (entry 1 in Table 2), or in any reactions of the other catalyst precursors. More convincing evidence for the importance of the outer-sphere phosphido mechanism shown in Figure 4, instead of this putative N-bound acrylonitrile pathway, is our observation of comparable catalytic activity for the hydrophosphination of *tert*-butyl acrylate using either complex **8** or **9** (entries 14 and 15 in Table 1). We would not expect the relatively sterically encumbered carbonyl group in this substrate to form an O-bound adduct, yet catalysis proceeds.

As mentioned above, in the growing literature of metal-catalyzed hydrophosphination of alkenes, the use of phosphine substrates that contain aryl substituents predominates. In this context, it is notable that the hydrophosphination of acrylonitrile by $HPCy_2$ is catalyzed by 10 mol % of complex **6** with DBU, giving 43% conversion to a single product after 48 h at room temperature (Table 2, entry 18). While this conversion is suspiciously close to that which we observed for the $HPPh_2$ reaction catalyzed by DBU alone, control reactions without Ru, and without either Ru or DBU, indicate that neither the base-catalyzed nor the thermal hydrophosphination reaction is occurring appreciably for this dialkyl substrate (Table 2, entries 19 and 20).

CONCLUSIONS

These results highlight the importance of coordinative unsaturation at the metal in encouraging inner-sphere, alkene insertion pathways for hydrophosphination and demonstrate the challenges in broadening the alkene substrate scope for late-metal catalysts. Currently we are examining the controlled introduction of secondary phosphine substrate in these reactions to identify conditions that may allow less activated alkenes to compete for binding and insertion at Ru in these systems, in addition to refining our choice of proton shuttle to encourage an inner-sphere mechanism. We also continue to probe the activity of this system for the hydrophosphination of activated alkenes and have begun to explore the reactions of other phosphines and other electron-deficient substrates in this context.

EXPERIMENTAL SECTION

General Details. Unless otherwise noted, all reactions and manipulations were performed under nitrogen in a glovebox or using conventional Schlenk techniques. Methanol was distilled from calcium hydride. THF was distilled from sodium under nitrogen and then stored over sodium/benzophenone, and was degassed by three freeze−pump−thaw cycles and vacuum-transferred before use. Dichloromethane, toluene, pentane, and hexane were degassed by sparging and then passed through columns of activated alumina in a solvent purification system. Deuterated solvents (Sigma-Aldrich) were stored over sodium/benzophenone (d_6-benzene) or calcium hydride (d_1-chloroform) and then freeze−pump−thaw degassed three times and vacuum-transferred before use, except for d_2-dichloromethane and d_8-THF, which were used as received in 1 g ampules. Unless otherwise specified, reagents were purchased from Sigma-Aldrich Canada and used as received (secondary phosphines, or dried and degassed using established procedures (other reagents). Diphenylphosphine was also purchased from Strem Chemicals as a 10% solution in hexanes; the concentration was checked against a known concentration of triphenylphosphine oxide by $^{31}P\{^1H\}$ NMR before use. $K[B(C_6F_5)_4]$ was purchased from Boulder Scientific Co. and was used as received. Pyridine hydrochloride was recrystallized ($CHCl_3$/ethyl acetate) before use. $Ru(\eta^5\text{-indenyl})Cl(PHR_2)PPh_3$ (**2**; R = Cy, Ph),[36] 2,6-lutidine hydrochloride,[37] $Ru(\eta^5\text{-indenyl})Cl(PPh_3)_2$,[38] and $Ru(\eta^5\text{-indenyl})(PPh_2)(NCPh)PPh_3$ (**8**)[21] were prepared using literature procedures.

NMR spectra were acquired on a Bruker AMX 360 spectrometer operating at 360.13 MHz for ^1H and 145.78 MHz for ^{31}P and a Bruker AVANCE 500 spectrometer operating at 500.13 MHz for ^1H, 202.43 MHz for ^{31}P, and 125.77 MHz for ^{13}C. Chemical shifts are reported in ppm at ambient temperature. ^1H chemical shifts are referenced to residual protonated solvent peak at 7.16 ppm (C_6D_5H). ^{13}C chemical shifts are referenced to C_6D_6 at 128.4 ppm and $CDCl_3$ at 77.5 ppm. ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane, and ^{31}P chemical shifts are reported relative to 85% H_3PO_4(aq).

Melting/decomposition temperatures were recorded using a Gallenkamp apparatus and are uncorrected. Microanalysis was performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada. IR spectra were recorded for KBr pellets on a PerkinElmer FTIR Spectrum 1000 spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was carried out by Rhonda Stoddard (group of Prof. Scott McIndoe) and Dr. Jingwei Luo at the University of Victoria on Waters QTOF Micromass and QTOF II instruments, using the following conditions: capillary voltage 3000 V, sample cone voltage 15 V, extraction voltage 0.5 V, source temperature 60 °C, desolvation temperature 120 °C, cone gas 100 L/h, desolvation gas 100 L/h, collision energy 2 V.

One-Pot Synthesis of Metallacycles 3a−c. *General Procedure.* Toluene (10 mL) was placed in a Schlenk flask containing $RuCl(\eta^5\text{-indenyl})(HPCy_2)(PPh_3)$ (**2**) and $KOBu^t$ (1.2 equiv) to give an orange suspension. With stirring the solution quickly became brown with a

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blue meniscus, and unsaturated substrate was added by gastight syringe. The mixture was stirred for 18 h to give a clear yellow or orange solution and then worked up as described below. $^{31}P\{^1H\}$ NMR data for all of the metallacycles and ^1H and ^{13}C NMR data for **3c** are given in the Supporting Information.

*Ru(η^5-indenyl)(κ^2-Bu^{n}CHCH$_2$PCy$_2$)(PPh$_3$) (**3a**).* Reagents: **2** (563 mg, 0.790 mmol), KOBu^t (137 mg, 1.22 mmol), 1-hexene (400 mL, 3.20 mmol). Solvent was removed under vacuum to give a yellow residue that was extracted with a 5/1 mixture of hexanes and toluene (25 mL) and filtered through Celite. The solvent volume was reduced under vacuum to 5 mL, and acetonitrile (15 mL) was added via cannula, resulting in the immediate precipitation of an orange powder. The product was isolated by filtration, washed with cold hexanes (3 × 5 mL), and dried under vacuum to give **3a** (393 mg, 0.52 mmol, 65%). ^1H and $^{31}P\{^1H\}$ NMR spectra indicate the exclusive formation of *syn*-**3a**. Our previous preparation of **3a** from the addition of 1-hexene to the isolated phosphido complex **1** gave 9% *anti*-**3a** upon workup.[6]

*Ru(η^5-indenyl)(κ^2-NCCHCH$_2$PCy$_2$)(PPh$_3$) (**3b**).* Reagents: **2** (317 mg, 0.445 mmol), KOBu^t (65 mg, 0.52 mmol), acrylonitrile (60 μL, 1.3 mmol). Solvent was removed under vacuum to give an orange residue that was extracted with a 5/1 mixture of hexanes and toluene (25 mL) and filtered through Celite. The solvent volume was reduced under vacuum to 1 mL, and acetonitrile (10 mL) was added via cannula, resulting in the immediate precipitation of a bright orange powder, **3b**. The complex was isolated by filtration, washed with cold hexanes (3 × 5 mL), and dried under vacuum (210 mg, 0.29 mmol, 66% yield). ^1H and $^{31}P\{^1H\}$ NMR spectra indicate the exclusive formation of *syn*-**3b**. Our previous preparation of **3b** from the addition of acrylonitrile to the isolated phosphido complex **1** gave 8% *anti*-**3b** upon workup.[6]

*Ru(η^5-indenyl)(κ^2-PhCHCH$_2$PCy$_2$)(PPh$_3$) (**3c**).* Reagents: **2** (307 mg, 0.431 mmol), KOBu^t (60 mg, 0.50 mmol), styrene (0.16 mL, 1.4 mmol). The solution was filtered through Celite, and the solvent was removed from the filtrate to give a red-orange powder (>99% *syn*-**3c**, 273 mg, 81% crude yield). A portion of the crude sample (120 mg, 0.15 mmol) was recrystallized from dichloromethane (5 mL) by slow layer diffusion of acetonitrile (~50 mL) to give analytically pure **3c** (94 mg, 80% yield, > 98% *syn* isomer). Anal. Found (calcd for $C_{47}H_{52}P_2Ru$): C, 71.97 (72.38); H, 6.63 (6.72). Mp: 164 °C. Note: unlike the case for **3a**,**b**, gentle heating of *syn*-**3c** in solution gave rapid epimerization, yielding a 1/1 *syn*/*anti* mixture within minutes at 60 °C.

Reactions of Metallacycles 3a−c with Protic Reagents. *NMR-Scale Protonolysis Experiments.* The reactions of complexes **3a−c** with pyridine hydrochloride, lutidine hydrochloride, and triethylamine hydrochloride were monitored by $^{31}P\{^1H\}$ NMR. Formation of the new mixed phosphine product Ru(η^5-indenyl)Cl{PCy$_2$(CH$_2$CH$_2$R′)}-PPh$_3$ (**4**, where R′ = Bu^n (**a**), CN (**b**), Ph (**c**)) was diagnosed by the appearance of new pairs of doublets in the $^{31}P\{^1H\}$ NMR spectra. In some cases, subsequent ligand redistribution reactions were observed, as diagnosed by the appearance of the signal due to Ru(η^5-indenyl)Cl(PPh$_3$)$_2$ (**1**). Full details of these experiments and $^{31}P\{^1H\}$ NMR data for complexes **4a−c** are included in the Supporting Information.

*Synthesis of Ru(η^5-indenyl)Cl(PCy$_2$(hexyl))PPh$_3$ (**4a**).* Pyridine hydrochloride (5.84 M in acetonitrile, 50 μL, 0.29 mmol) was added to a solution of Ru(η^5-indenyl)(κ^2-Bu^{n}CHCH$_2$PCy$_2$)PPh$_3$] (**3a**; 212 mg, 0.279 mmol) in toluene (10 mL) in a Schlenk flask. The resulting red solution was stirred for 24 h at room temperature. Removal of the solvent under vacuum gave a red solid, which was extracted with pentane (3 × 5 mL) and transferred by cannula to another Schlenk. The solvent was removed under vacuum, leaving pure **4a** (50 mg, 23% yield). $^{31}P\{^1H\}$ NMR analysis showed that ligand redistribution occurs readily in solution; LIFDI-MS analysis of a freshly prepared toluene solution of the product confirmed the identity of **5d** and also showed small amounts of **1** and the free PCy$_2$(hexyl) ligand (see the Supporting Information).

*Reaction of **4a** with HPCy$_2$.* Pyridine hydrochloride (5.84 M in acetonitrile, 4 μL, 0.023 mmol) was added to 12 mg (0.016 mmol) of **3a** dissolved in d_6-benzene (0.4 mL) to generate **4a** in situ, as determined by $^{31}P\{^1H\}$ NMR. HPCy$_2$ (0.4 M in hexane, 0.2 mL, 5 equiv) was added, and the mixture was monitored by $^{31}P\{^1H\}$ NMR. Complex **4a** was completely consumed after 24 h, giving a mixture of products that includes Ru(η^5-indenyl)Cl(PCy$_2$H)(PPh$_3$) (**2**), Ru(η^5-indenyl)Cl{PCy$_2$(CH$_2$CH$_2$Bu^n)}$_2$, and several other phosphine-containing products that have not yet been identified (see Supporting Information).

Reactions of [Ru(η^5-indenyl)(NCMe)(PCy$_2$H)(PPh$_3$)$_2$][PF$_6$] (5).[39] *Reaction of **5** with DBU.* DBU (350 mg, 2.3 mmol, 100 equiv) was added to a solution of finely ground complex **5** (20 mg, 0.023 mmol) in d_1-chloroform in a J. Young NMR tube. The solution turned dark green-blue, and an initial $^{31}P\{^1H\}$ NMR showed signals due to complex **1**[5a] as the major product. The complex subsequently decomposed to a variety of unidentified products in this solvent.

*Reaction of **5** with DBU and Acrylonitrile.* DBU (18 mg, 0.12 mmol, 5 equiv) and acrylonitrile (6 mg, 0.1 mmol, 5 equiv) were added to a solution of finely ground complex **5** (20 mg, 0.023 mmol) in a 70/30 mixture of d_6-benzene and PhF in a J. Young NMR tube. The solution gradually changed color from yellow to orange, and $^{31}P\{^1H\}$ NMR confirmed the slow formation of metallacycle **3b**.[6]

Synthesis of Catalyst Precursors 6, 7, and 9. ^1H and ^{13}C NMR assignments are given in the Supporting Information.

*[Ru(η^5-indenyl)(NCPh)(PPh$_3$)$_2$][B(C$_6$F$_5$)$_4$] (**6**).* Benzonitrile (0.35 mL, 3.4 mmol) was added to an orange suspension of **2** (0.875 g, 1.13 mmol) and KB(C$_6$F)$_4$ (0.809 g, 1.13 mmol) in methanol (25 mL). The resulting orange mixture was stirred for 1 day, during which time it turned yellow with a yellow precipitate. The solution was filtered, and the solid was dried under vacuum. It was then dissolved in dichloromethane, filtered to remove KCl, and layered with methanol, which gave **6** as an orange crystalline solid (1.25 g, 70% yield). Anal. Found (calcd for $C_{76}H_{42}NP_2RuBF_{20}$): C, 59.81 (59.94); H, 2.64 (2.78); N, 0.85 (0.92). IR (KBr, cm^{-1}): 2228 (w, ν_{CN}). LR-ESI-MS (CH$_2$Cl$_2$, *m*/*z*): 844.35 (M$^+$, 100%), 741.34 ([M − NCPh]$^+$, 40%). Dec pt: 172−175 °C. $^{31}P\{^1H\}$ NMR (202.43 MHz, d_2-dichloromethane): δ 46.9 (s, PPh$_3$).

*[Ru(η^5-indenyl)(NCPh)(PPh$_2$H)(PPh$_3$)][B(C$_6$F$_5$)$_4$] (**7**).* The procedure described for **6** was followed, using benzonitrile (0.87 mL, 8.40 mmol), Ru(η^5-indenyl)(Cl)(PPh$_2$H)(PPh$_3$) (0.982 g, 1.40 mmol), and KB(C$_6$F$_5$)$_4$ (1.00 g, 1.40 mmol) in methanol (25 mL). The reaction mixture was stirred for 3 days before workup, which gave **7** as an orange crystalline solid (1.28 g, 63% yield). Anal. Found (calcd for $C_{70}H_{38}NP_2RuBF_{20}$): C, 58.29 (58.11); H, 2.46 (2.65); N, 0.90 (0.97). IR (KBr, cm^{-1}): 2322 (w, ν_{PH}), 2237 (w, ν_{CN}). LR-ESI-MS (CH$_2$Cl$_2$, *m*/*z*): 768.07 (M$^+$, 100%). Dec pt: 173−175 °C. $^{31}P\{^1H\}$ NMR (202.43 MHz, *d*-chloroform): δ 56.3 (d, 42, PPh$_3$), 35.0 (d, PPh$_2$H).

*Ru(η^5-indenyl)(PPh$_2$)(PPh$_2$H)(PPh$_3$) (**9**).* KO^{t}Bu (44 mg, 0.40 mmol) was added to an orange solution of Ru(η^5-indenyl)(Cl)-(PPh$_2$H)(PPh$_3$) (232 mg, 0.33 mmol) and HPPh$_2$ (0.17 mL, 0.99 mmol, 3 equiv) in toluene (30 mL) in a Schlenk flask. The solution turned deep purple and was stirred for 1 h. The solution was then filtered through Celite to remove KCl and HO^{t}Bu. The solvent was removed under vacuum to give a purple solid, which was washed with pentane (3 × 10 mL) and dried (190 mg, 68% yield). We have so far been unable to obtain this complex free of minor impurities (see the Supporting Information for NMR spectra); thus, it has not been submitted for microanalysis. IR (KBr, cm^{-1}): 2310 (w, ν_{PH}). Dec pt: 178−180 °C. $^{31}P\{^1H\}$ NMR (202.43 MHz, d_8-THF): δ 49.1 (d, 35, PPh$_3$), 42.6 (dd, PPh$_2$H), 40.5 (d, 15, PPh$_2$).

X-ray Diffraction Studies of Complexes 6 and 7. Crystals of **6** were grown from a solution of the compound in benzene, while crystals of **7** were grown by layering methanol onto a dichloromethane solution of the compound. Suitable crystals were coated with a thin layer of Paratone-N and then mounted on a Bruker PLATFORM diffractometer equipped with an APEX II CCD area detector,[40] with the crystals cooled to −80 °C under a cold nitrogen gas stream. Diffraction measurements were made using Mo Kα radiation (λ = 0.71073 Å). The structure of **6** was solved with the direct methods program SHELXTL-2014,[41a] while the structure of **7** was determined using a Patterson search for heavy atoms followed by structure expansion, as implemented in the DIRDIF-2008[42] program system. The structure refinements were completed using the least-squares

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refinement program SHELXL-2014.[41b] The phosphorus-bound hydrogen atom in **7** was located from a difference Fourier map, and its coordinates and isotropic displacement parameter were freely refined. All other hydrogens were generated in idealized positions on the basis of the sp^2 or sp^3 geometries of their attached carbons and given isotropic displacement parameters 120% of the U_{eq} values for their parent C atoms.

Catalyst Screening and Associated Control Reactions. *General Procedure for Catalytic Runs.* To 1 equiv of catalyst (0.02 mmol) in a J. Young NMR tube was added 1 equiv of DBU (0.2 mL, 0.1 M in THF), 10 equiv of alkene (0.2 mL, 1.0 M in THF), and 10 equiv of HPR_2 (0.2 mL, 1.0 M in THF) and d_6-benzene (0.2 mL). Each reaction was performed in triplicate; conversions and product ratios were determined from relative integrations of the product and free secondary phosphine signals in $^{31}P\{^1H\}$ NMR spectra obtained using a gated decoupled experiment with a relaxation delay of 55 s.

General Procedure for Control Reactions. To 0.2 mL of C_6D_6 in a J. Young NMR tube was added two or more of 0.02 mmol of a Ru catalyst, 0.2 mL of HPR_2, alkene (1.0 M in THF, 10 equiv), or DBU (0.1 M in THF, 1 equiv). In reactions where one or two reagents were left out, the corresponding volume of THF (0.2 or 0.4 mL) was added to maintain the same concentrations as would be present in the catalytic reactions described above. The reactions were monitored by $^{31}P\{^1H\}$ NMR, using the quantitative pulse sequence where necessary.

The results of these reactions are shown in Table 2 and/or described in the text, and representative spectra are included in the Supporting Information.

Thermolysis of Complex 9 Monitored by $^{31}P\{^1H\}$ NMR. A solution of **9** (20 mg, 0.024 mmol) in d_8-toluene was placed in a flame-sealable NMR tube, degassed by three freeze−pump−thaw cycles, and sealed under vacuum. An initial $^{31}P\{^1H\}$ NMR spectrum was obtained. The solution was heated at 60 °C in an oil bath and removed periodically for monitoring by $^{31}P\{^1H\}$ NMR. After 96 h, approximately 50% of **9** had decomposed, giving the ortho-metalated complex $[Ru(\eta^5\text{-indenyl})\{\kappa^2\text{-}(o\text{-}C_6H_4)PPh_2\}(PPh_2H)]$ as well as free PPh_3 and a corresponding complex tentatively identified as $Ru(\eta^5\text{-indenyl})(PPh_2)(PPh_2H)_2$ (see the Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00835.

Crystallographic data for complexes **6** and **7** (CIF)
Additional experimental details, including NMR spectra of new compounds and representative product mixtures, and crystallographic data for complexes **6** and **7** (PDF)

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Notes

The authors declare no competing financial interest.
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attributed to the high reactivity of the coordinatively unsaturated cationic product resulting from step **D** in Figure 2 and resulting noninnocence of the solvent. Future experiments will exploit the benzene-soluble $B(C_6F_5)_4^-$ counterion.

(17) Literature pK_a values for $HPPh_2$ vary considerably, ranging from 21.7 (THF, ref 10) to 22.9 (calculated for DMSO, ref 17a) to 38 ± 4 (THF, ref 17b). Importantly, where values for $HPCy_2$ are also noted, they are inevitably at least 7−14 pK_a units higher (vide supra). (a) Li, J. N.; Liu, L.; Fu, Y.; Guo, Q. X. *Tetrahedron* **2006**, *62*, 4453−4462. (b) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171.

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(24) The structurally similar half-sandwich complexes Ru(η^5-Cp*)(PPh_2)(PP), where PP is a chelating diphosphine ligand, either *cis*-1,2-bis(diphenylphosphino)ethylene or 1,2-bis(diphenylphosphinobenzene), reported by Morris in ref 14 show initial TOFs of 30−60 h^{-1}, about 1 order of magnitude higher than the values we observe, but the catalysts deactivate after 1 h. The higher initial activity could be due simply to the stronger donating ability of Cp* relative to indenyl, which should render the phosphido ligand more basic/nucleophilic (vide infra). Glueck's Pt diphosphine complexes (ref 23) show activities closer to those which we observe (10 h^{-1}), for reactions carried out at 50 °C instead of room temperature.

(25) Other literature examples of the base-mediated reaction of $HPPh_2$ with acrylonitrile have exploited bases much stronger than DBU in stoichiometric quantities. Two reports of the use of 50% NaOH(aq) (refs 25a and b) cite the much earlier use of these conditions for the reactions of H_2PPh with acrylonitrile.[25] Another example (ref 25d) uses NEt_4OH for the reaction of $HPPh_2$ with activated alkenes other than acrylonitrile. (a) Li, Y. Z.; Li, Z. M.; Li, F.; Wang, Q. R.; Tao, F. G. *Tetrahedron Lett.* **2005**, *46*, 6159−6162. (b) Dibowski, H.; Schmidtchen, F. P. *Tetrahedron* **1995**, *51*, 2325−2330. (c) Rauhut, M. M.; Hechenbleikner, I.; Currier, H. A.; Schaefer, F. C.; Wystrach, V. P. *J. Am. Chem. Soc.* **1959**, *81*, 1103−1107. (d) Wiese, B.; Knuhl, G.; Flubacher, D.; Priess, J. W.; Ulriksen, B.; Brodner, K.; Helmchen, G. *Eur. J. Org. Chem.* **2005**, *2005*, 3246−3262.

(26) Literature $\delta(^{31}P)$ data for product phosphines in d_6-benzene: −15.3 ppm ($Ph_2PCH_2CH_2CN$, ref 4b), −20.1 ppm ($Ph_2PCH(CN)CH_3$, ref 14), −14.7 ($Ph_2PCH_2CH_2CO_2Bu^t$, ref 4b). Under our conditions (3/1 THF/d_6-benzene), we observe signals within ±1 ppm of these values. We found no literature value for $Ph_2PCH(CO_2Bu^t)CH_3$ but do observe a very tiny peak at −23.3 ppm that we have tentatively assigned to this branched isomer. For the reaction of acrylonitrile with $HPCy_2$ we observe one major product with $\delta(^{31}P)$ at −2.0 ppm that we have assigned to the linear product; $^1H/^{31}P$ HMBC NMR confirms the connectivity of this tertiary P to Cy and other alkyl groups (see the Supporting Information). We also see three tiny signals in the range −2 to −10 ppm; we presume one of these is due to the branched product $Cy_2PCH(CN)CH_3$ but have not identified the other minor impurities.

(27) We carried out a control reaction under conditions comparable to those for the catalyst screening reactions shown in Table 2, in which 10 equiv of $HPPh_2$ was added to complex **8** in the absence of acrylonitrile or DBU. This reaction shows complete conversion to complex **9** within minutes of preparing the sample (see Figure S27 in the Supporting Information).

(28) As noted in the Introduction, other late metal phosphido complexes also undergo such Michael additions at activated alkenes. See for examples refs 4a−c, 8, 9, and 14.

(29) See the Supporting Information, including Figures S29−S34, for further discussion of, and tentative structural assignments for, the spectroscopically observed "catalyst resting states" for the catalytic reactions of acrylonitrile with $HPPh_2$.

(30) We also do not see signals due to metallacycles **3** in control reactions that omit the DBU cocatalyst (entries 10, 11, and 13 in Table 2).

(31) We added 10 equiv of acrylonitrile to complex **8** in 3/1 THF/d_6-benzene in the absence of $HPPh_2$ or DBU, in an attempt to observe the corresponding metallacycle, which had not previously been prepared. However, the NMR sample solidified. We suspect this basic phosphido complex may promote polymerization (or telomerization, see refs 4a and b) of the acrylonitrile under these conditions. We were unable to obtain NMR spectra for this solid to see if any metallacycle forms under these conditions.

(32) As described in ref 21, heating a sealed sample of Ru(η^5-indenyl)(PPh_2)(CO)(PPh_3) in d_8-toluene to 60 °C for up to 90 h gave no reaction; none of the ortho-metalated complex Ru(η^5-indenyl){κ^2-(*o*-C_6H_4)PPh_2}(PPh_2H) that would result from CO dissociation was observed.

(33) For complexes **6** and **7**, the DBU is needed to initiate catalysis (either inner or outer sphere) by deprotonating coordinated secondary phosphine; control reactions shown in entries 8 and 9 in Table 2 indicate that hydrophosphination of acrylonitrile is *not* catalyzed by these complexes in the absence of DBU.

(34) Yet another mechanistic possibility has been proposed for the Pd-catalyzed hydrophosphination of alkynes and for Rh-catalyzed hydrophosphination of dimethyl fumarate and ethylene (ref 4h), which involves oxidative addition of the P−H bond, followed by insertion of the unsaturated substrate into the M−H bond, and subsequent reductive elimination of a P−C bond. Such a mechanism is unlikely to be occurring in this Ru system, since we see no evidence in any of our reactions for the oxidative addition of a P−H bond (cycles involving such Ru(II)/Ru(IV) oxidation state changes are rare), and no Ru−H intermediates are observed. Kazankova, M. A.; Efimova, I. V.; Kochetkov, A. N.; Afanas'ev, V. V.; Beletskaya, I. P.; Dixneuf, P. H. *Synlett.* **2001**, 497−500. Ananikov, V. P.; Makarov, A. V.; Beletskaya, I. P. *Chem. - Eur. J.* **2011**, *17*, 12623−12630.

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