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Iminophosphanes: Synthesis, Rhodium Complexes, and Ruthenium(II)-Catalyzed Hydration of Nitriles

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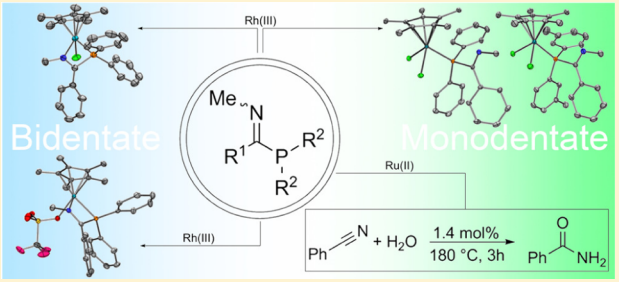
Supporting Information

ABSTRACT: Highly stable iminophosphanes, obtained from alkylating nitriles and reaction of the resulting nitrilium ions with secondary phosphanes, were explored as tunable P-monodentate and 1,3-P,N bidentate ligands in rhodium complexes. X-ray crystal structures are reported for both κ^1 and κ^2 complexes with the counterion in one of them being an unusual anionic coordination polymer of silver triflate. The iminophosphane-based ruthenium(II)-catalyzed hydration of benzonitrile in 1,2-dimethoxyethane (180 °C, 3 h) and water (100 °C, 24 h) and under solvent free conditions (180 °C, 3 h) results in all cases in the selective formation of benzamide with yields of up to 96%, thereby outperforming by far the reactions in which the common 2-pyridyldiphenylphosphane is used as the 1,3-P,N ligand.



INTRODUCTION

Hybrid ligands are important in catalysis, as they enable ligand- and metal-based reactivity in bifunctional systems.[1,2] In particular, P,N ligands are of interest because of the presence of both soft phosphorus and hard nitrogen donor sites.[3] Of the various topologies,[4−7] 1,3-P,N ligands have shown ample applicability in transition-metal-based catalysis (Figure 1).

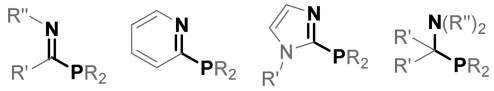


Figure 1. 1,3-P,N ligand systems.

The C_1 spacer provides optimal separation[8] for metal coordination at nitrogen,[9] phosphorus,[10,11] or both atoms,[11] as well as enabling the formation of homo-[12] and hetero-bimetallic[13] complexes for metal activation, photoluminescence, and cooperative metal−metal systems (Figure 2).[13a,14]

Exemplary reactions that make use of 1,3-P,N ligands are the Ru-catalyzed hydration of nitriles,[10a,11a,h] the Pd-catalyzed carbonylation of alkynes,[10c,11d,e] Pd-catalyzed Buchwald−Hartwig and Suzuki−Miyaura cross-coupling reactions,[15] dinuclear Pd- and [Fe-Rh]-catalyzed carbonylation of alcohols,[12d,e,13c] the Ru- and Au-catalyzed hydration of alkynes,[10d,e] the Ru-catalyzed transfer hydrogenation of ketones and aldehydes,[11b,g] the Ru-catalyzed isomerization of alkenes,[10b] the Ru-catalyzed and dinuclear Rh-catalyzed hydrogenation of alkenes,[11f,12b] the Rh-, Ir-, and [Ru−Rh]-catalyzed hydroformylation of alkenes,[11c,13a,d] and the Cr-catalyzed tri- and tetramerization of ethylene,[11i] whereas Cu^I_2 and $[Au^I_3\text{-}Ag^I]$ complexes have been used in photoluminescence.[12a,c,13b] A popular ligand in the complexes used for these reactions is 2-pyridyldiphenylphosphane ($PyPPh_2$),[3,16] even though it has limited flexibility for steric and electronic tuning of particularly the N-donor site. Replacement of the pyridine group by an imine or amine functionality provides 1,3-P,N ligands with more opportunities to tune the properties of their derived catalysts.

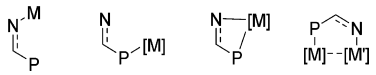


Figure 2. 1,3-P,N coordination modes.

Recently, we reported a simple methodology, based on nitrilium ions, to synthesize iminophosphanes (IUPAC: *c*-phosphanylimines) and anionic phosphaamidinates that carry different substituents at all three C, N, and P sites (Scheme 1).[17] Shortly thereafter Hanton, Dyer, and co-workers reported

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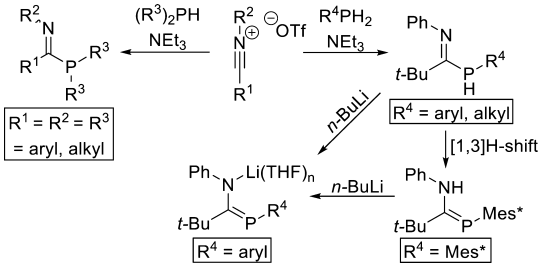
Scheme 1. Synthesis of Iminophosphanes and Phosphaamidinates from Nitrilium Ions



neutral ligands by condensing silylated phosphanes and imidoyl chlorides, but this method is intrinsically more limited.[11i] These 1,3-P,N ligands coordinate to Au,[17] Rh,[17] Ir,[17b] and Cr[11i] complexes. The iminophosphanes display dynamic κ^1 and κ^2 coordination behavior in the case of Rh(III), while 2-pyridylphosphanes generally give exclusively κ^1 Rh complexes.[18a−c]

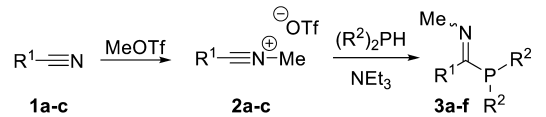
In the present study we expand on the synthesis of iminophosphanes to display the diversity of the nitrilium ion methodology, report on the chelation to Rh(III) to further exploit the intricacies of κ^1 versus κ^2 coordination, and examine the performance of the iminophosphane versus the $PyPPh_2$ ligand for the Ru(II)-catalyzed hydration of nitriles. The last process, first reported in 1986[19] and used for the production of polyacrylates and pharmaceuticals,[19−21] was chosen because of the role of the N-donor site in activating water in the catalytic cycle.

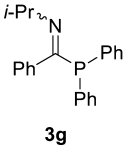
RESULTS AND DISCUSSION

The synthesis and stability of new iminophosphanes with relatively small substituents is presented first. Next, the coordination to Rh(III) is examined. This is followed by an assessment of the performance of the ligands in the Ru(II)-catalyzed hydration of nitriles.

Ligands. A set of iminophosphanes (**3a−f**) with different electronic properties but similar steric features was prepared from nitrilium triflates **2** (Scheme 2). The procedure is

Scheme 2. Synthesis of Iminophosphanes 3





3	R1	R2	Yield	E/Z
a	Ph	Ph	91	71/29
b	4-CH_3-C_6H_4	Ph	75	83/17
c	4-CF_3-C_6H_4	Ph	85	45/55
d	Ph	3-CF_3-C_6H_4	46	83/17
e	Ph	3-CH_3-C_6H_4	77	68/32
f	Ph	4-CH_3-C_6H_4	53	76/24

3g

analogous to the protocol we reported recently, the difference being that here nitriles **1** are directly alkylated to provide the ion, whereas previously we obtained the ions from imidoyl chlorides.[17] The choice of synthetic approach depends on the N substituent: with *i*-Pr or larger alkyl groups, imidoyl chlorides are the starting point, sometimes necessitating stabilization of the resulting nitrilium ions with pyridine bases,[17c] but smaller groups are only accessible by nitrile alkylation.[22] Thus, treating **1** with MeOTf gave the corresponding *N*-methyl nitrilium triflates **2** (R = Ph (**a**), 4-CH_3-C_6H_4 (**b**), 4-CF_3-C_6H_4 (**c**)). The reaction with **1b** was carried out in toluene at ambient temperature to provide after 5 days white crystalline **2b** (62%). Methylations of the less nucleophilic **1a,c** were performed without solvent over an 18 h period; in the case of **1c** a slightly elevated reaction temperature of 45 °C was used to melt the nitrile. Crystallization of the crude products provided nitrilium salts **2a** (DCM/Et_2O) and **2c** (DCM/pentane) as white solids in 86% and 69% yields, respectively.

Dropwise addition of diphenylphosphane and its 3-methyl, 3-CF_3, and 4-methyl derivatives to a DCM solution of nitrilium triflates **2a−c** at −78 °C, followed by deprotonation with triethylamine at room temperature, resulted in the quantitative formation of iminophosphanes **3a−f** (Scheme 2). Et_2O extraction, filtration over alumina, and crystallization provided the products in 46−91% as *E*/*Z* mixtures, as determined by their ^{31}P NMR chemical shifts (i.e., **3a** 7.8 (*E*), −7.6 (*Z*); **3b** 7.6 (*E*), −8.0 (*Z*); **3c** 8.2 (*E*), −7.7 (*Z*); **3d** 5.9 (*E*), −8.5 (*Z*); **3e** 8.3 (*E*), −7.5 (*Z*); **3f** 6.3 (*E*), −8.8 (*Z*)) with assignments based on related ones reported earlier.[17b] The *E*/*Z* ratios were found to be sensitive to the experimental setup (e.g., concentration), which is in agreement with the calculated very small energy differences (ωB97X-D/6-31+G(d,p); $|\Delta E_{E\text{-}Z}|$ = 0.19−0.78 kcal mol^{-1})[23] as well as similar behavior reported for related systems;[17] **3g** was included for its different N substituent (*i*-Pr versus Me).[17b]

Ligand Stability. Exploring the applicability of iminophosphanes in transition-metal-catalyzed reactions, such as the hydration of nitriles (vide infra), requires these P,N ligands to be stable toward water, whereas it is quite conceivable that they are prone to hydrolysis to the corresponding diarylphosphanes and amides. It is then comforting to see, using ^{31}P NMR monitoring, that the stability of *E*-/*Z*-**3a** in acetone toward hydrolysis by degassed water over a period of 211 h showed only slight degradation, which was attributed to oxidation to [**3a**(O)] by air rather than hydrolysis (Figure 3). The oxidation

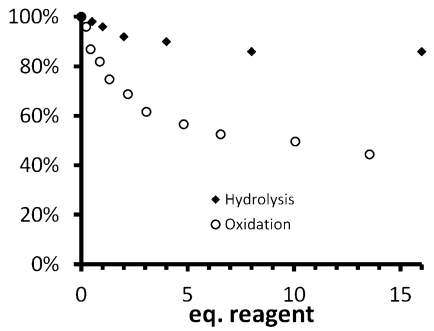


Figure 3. Sensitivity of **3a** (%) toward hydrolysis (reagent H_2O (degassed)) and oxidation (reagent O_2 (in air)).

sensitivity of **3a** was confirmed in a separate assessment (see Supporting Information). Similar results were obtained for **3b,c** (see Supporting Information). The presence of 0.10 equiv of triflic acid did not catalyze the hydrolysis of **3a**. Exposure of **3a** to triflic acid at room temperature gave only N-protonated iminophosphane without any degradation over a 46 h period. This indicates that iminophosphanes are reasonably rugged ligands.

Rhodium Coordination. The chelation of the iminophosphanes toward rhodium was explored next. Recently, we found

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that ligands bulkier than **3a−f** give P-monodentate complexes with Au(I), bidentate complexes with Ir(III), and both κ^1 and κ^2 complexes with Rh(III), of which only bidentate complexes were isolable as the major products.[17b] We wondered whether we could make monodentate Rh complexes the prevalent product, which is of interest for cooperative Rh(III) catalysis,[10,11,13d,24] without relying on steric effects.[25] We also wondered how silver triflate, commonly added in excess in Rh(III) catalysis,[24b,c] plays a role beyond the formation of bidentate complexes by single Cl abstraction. To address these issues, we focus on the chelation of **3a,c,e**.

Treating *E*-/*Z*-**3a** in DCM with 1/2 equiv of $[RhCp^*Cl_2]_2$ at room temperature yielded two products in a 96:4 ratio (Scheme 3). The major product ($\delta(^{31}P)$ 34.5 ppm; $^1J_{P,Rh}$ = 145.7 Hz), isolated as an orange solid (89%), is assigned to the *E* isomer of monodentate Rh complex **4a**, in analogy to reported in situ Rh complexes.[17c] The minor product ($\delta(^{31}P)$ −5.1 ppm; $^1J_{P,Rh}$ = 113.4 Hz) is likely bidentate complex **5a** because of its similarity in ^{31}P NMR data to related, bulkier Rh complexes.[17c] Crystallization of **4a** by slow diffusion of pentane into a DCM/Et_2O solution provided crystals suitable for an X-ray structure determination. The molecular structure confirms P-monodentate coordination and the *E* conformation for the imine group (Figure 4), thereby illustrating the ease of *Z* to *E* isomerization of the ligand.[17c] The N1−C1 bond length of 1.2738(17) Å is typical for a C=N bond and the 1.8659(13) Å long P1−C1 bond is normal for a P−alkyl single bond; the Rh1−P1−C1−N1 torsion angle amounts to −56.15(11)°, with H-bonding interactions between Cp*−CH_3 groups and the N lone pair. The 2.3222(4) Å Rh1−P1 bond length of **4a** is similar to that of the 2-pyridylphosphanyl Rh(III) κ^1 complexes.[18a−c]

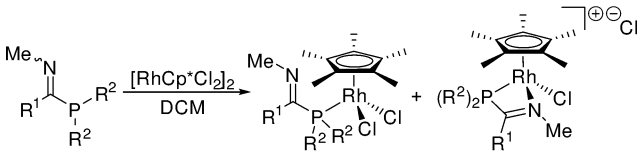
P-monodentate complexes **4c** ($\delta(^{31}P)$ 35.4 ppm, $^1J_{P,Rh}$ = 147.4 Hz) and **4e** ($\delta(^{31}P)$ 34.7 ppm, $^1J_{P,Rh}$ = 145.8 Hz) were prepared likewise from **3c,e** and isolated in 69% and 92% yields, respectively (Scheme 3). The molecular structure of **4e**, obtained by a single-crystal X-ray structure determination, reveals structural parameters with bond lengths Rh1−P1 = 2.3196(6) Å, N1−C1 = 1.269(3) Å, and P1−C1 = 1.870(2) Å and a −53.92(19)° Rh1−P1−C1−N1 torsion angle that are comparable to those of **4a** (Figure 4). ^{31}P NMR analysis of the two reactions showed only in the case of **3e** formation of a byproduct (6%) that is assigned to P,N bidentate complex **5e** ($\delta(^{31}P)$ −12.1 ppm, $^1J_{P,Rh}$ = 114.7 Hz).

The reproducible **4**:**5** ratios indicate that the small extent or absence of observed bidentate complexes depends to a degree on the aromatic substituent. In comparison to the *C*- and *P*-phenyl groups, the *m*-tolyl substituent at carbon (**e**) enhances bidentate formation slightly (from 4 to 6%), while the *p*-CF_3-phenyl group at phosphorus (**c**) blocks it (Scheme 3). This trend concurs with the N-donor strength calculated at ωB97X-D/6-31+G(d,p) (Def2-TZVP for Rh) from the energy required to transform cationic complex **5** from a κ^1 to a κ^2 arrangement (Scheme 4);[17b,23] a comparison between neutral **4** and ionic $\mathbf{5}^+$ is not feasible. The Rh−N bond strengths of **5a,c,e** amount to −14.7, −13.4, and −15.2 kcal mol^{-1}, respectively, with corresponding N lone pair orbital energies of −11.2, −11.4, and −11.0 eV. These data support the notion that the selective formation of only P-chelated complexes of 1,3-P,N ligands can be controlled by changing the N-donor strength.

Of course, the 1,3-P,N ligands can also undergo clean chelation with rhodium as shown before, but under more forcing conditions. For example, treating **4** with 1 equiv of silver triflate yielded bidentate complex **6** quantitatively (Scheme 5).

These ionic complexes, containing a triflate counteranion instead of a chloride anion as in **5**, were isolated as bright orange solids and identified by their ^{31}P NMR characteristics (**6a**, −9.1 ppm, $^1J_{P,Rh}$ = 113.4 Hz; **6c**, −5.0 ppm, $^1J_{P,Rh}$ = 115.0 Hz; **6e**, −8.6 ppm, $^1J_{P,Rh}$ = 113.4 Hz). When **4a** was treated with an excess of 4 equiv of AgOTf,[24b,c] a yellow solid resulted (**7a**, 80%) having a ^{31}P NMR chemical shift (−9.9 ppm; $^1J_{P,Rh}$ = 111.8 Hz) which differs from that of **6a** (Scheme 5). Single-crystal X-ray structure determinations confirm the bidentate nature of both complexes (Figure 5) and reveal that the excess of AgOTf caused the exchange of rhodium's coordinated chloride for an OTf group, without affecting the P,N ligand.

Scheme 3. Synthesis of Mono- and Bidentate Rh(III) Complexes 4 and 5



	R^1	R^2	4:5
a	Ph	Ph	96:4
c	4-CF_3-C_6H_4	Ph	100:0
e	Ph	3-CH_3-C_6H_4	94:6

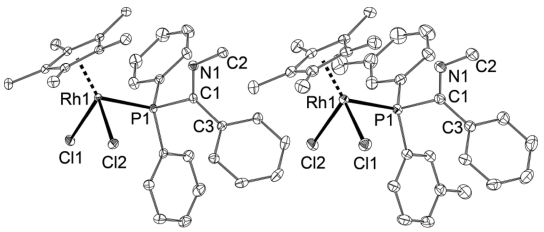
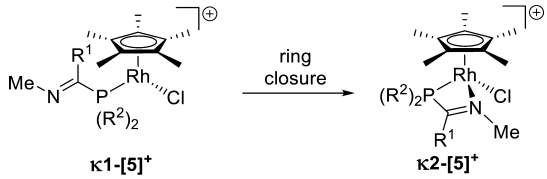


Figure 4. Displacement ellipsoid plots of rhodium complexes **4a** (left) and **4e** (right) at the 50% probability level. Hydrogen atoms and DCM are omitted for clarity. Selected bond lengths (Å) and angles (deg): **4a**, Rh1−P1 = 2.3222(4), Rh1−Cl1 = 2.4056(3), Rh1−Cl2 = 2.4008(4), P1−C1 = 1.8659(13), N1−C1= 1.2738(17), N1−C2 = 1.4634(17), C1−C3 = 1.4946(17), N1−C1−P1 = 112.72(9), Rh1−P1−C1−N1 = −56.15(11); **4e**, Rh1−P1 = 2.3196(6), Rh1−Cl1 = 2.4013(6), Rh1−Cl2 = 2.4011(6), P1−C1 = 1.870(2), N1−C1= 1.269(3), N1−C2 = 1.469(3), C1−C3 = 1.493(3), N1−C1−P1 = 113.62(18), Rh1−P1−C1−N1 = −53.92(19).

Scheme 4. DFT Analysis of the N-Donor Capacity of 3a,c,e



	R^1	R^2	$\Delta E_{(ring\ closure)}$ [kcal/mol]	$\Delta E_{(N\text{-}LP)}$ [eV]
a	Ph	Ph	-14.7	-11.2
c	4-CF_3-C_6H_4	Ph	-13.4	-11.4
e	Ph	3-CH_3-C_6H_4	-15.2	-11.0

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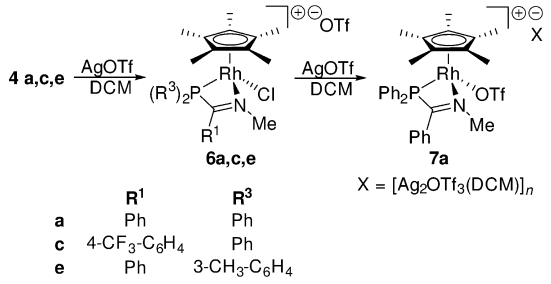
Scheme 5. Bidentate Coordination of 3 to Rh(III)



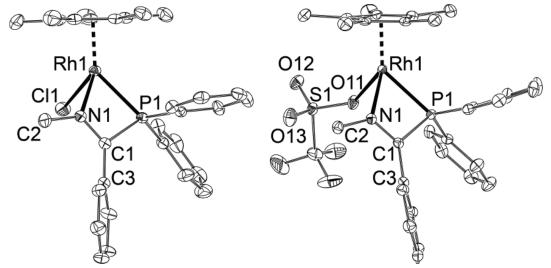


Figure 5. Displacement ellipsoid plots of cationic rhodium complexes **6a** (left) at the 30% probability level and **7a** (right) at the 50% probability level. Hydrogen atoms and counterions (triflate and $[Ag_2OTf_3(DCM)]_n^-$, respectively) are omitted for clarity. Selected bond lengths (Å) and angles (deg): for **6a**, Rh1−P1 = 2.3123(14), Rh1−N1 = 2.106(4), Rh1−Cl1 = 2.3728(13), P1−C1 = 1.842(5), N1−C1 = 1.274(7), N1−C2 = 1.466(7), C1−C3 = 1.461(7), N1−Rh1−P1 = 66.27(12), N1−C1−P1 = 100.4(4); **7a**, Rh1−P1 = 2.3328(7), Rh1−N1 = 2.126(2), Rh1−O11 = 2.1957(18), P1−C1 = 1.844(3), N1−C1 = 1.294(3), N1−C2 = 1.466(3), C1−C3 = 1.471(4), S1−O11 = 1.4711(19), S1−O12 = 1.433(2), S1−O13 = 1.429(2), N1−Rh1−P1 = 67.02(6), N1−C1−P1 = 102.29(18).

The molecular structure of **6a** shows Rh1−P1, Rh1−N1, and Rh1−Cl1 bond lengths of respectively 2.3123(14), 2.106(4), and 2.3728(13) Å and an acute N1−C1−P1 bond angle of 100.4(4)°. The structural features of **7a** resemble those of **6a** and other bidentate 1,3-P,N Rh(III) complexes,[17,18a,b,d] except for its triflate group with an Rh1−O11 bond length of 2.1957(18) Å that is similar to those reported for monodentate Rh(III)−triflate bonds.[26] Expectedly, the S1−O11 bond is elongated with respect to the S1−O12 and S1−O13 bonds: i.e., 1.4711(19), 1.433(2), and 1.429(2) Å, respectively.

The counterion of **7a** is a coordination polymer of silver triflate (Figure 6). Whereas aggregates of Ag(I) sulfonates are known,[27] the present structure is, to the best of our knowledge, the first of its kind in an organometallic complex. The molecular structure shows a linear chain with alternating C_s-symmetric dinuclear Ag(I) units (Ag1−Ag2 = 3.0410(3) Å) that are bridged by triflate anions. Each Ag atom has a distorted-octahedral geometry with bi-, tri-, and tetradentate coordinating triflate groups labeled as 2, 3, and 4 in Figure 6 (right); the Ag−O bond distances range from 2.321(2) to 2.509(2) Å.[27] The weak coordination of DCM (Ag1−Cl1 = 2.9042(9) Å) completes the octahedral coordination sphere of Ag1.[28]

Application in Catalytic Nitrile Hydration. Having established simple synthetic protocols for highly stable iminophosphanes and having demonstrated their ability to function as P monodentate and P,N bidentate ligands, we set out to explore their potential as hydration catalysts for nitriles. This reaction was chosen to compare iminophosphanes to the

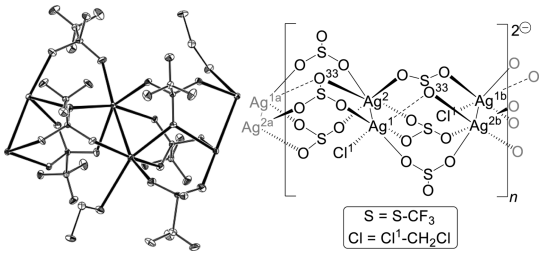


Figure 6. Displacement ellipsoid plot of a dimeric unit of the $[Ag_2OTf_3(DCM)]_n$ counterion of **7a** at the 20% probability level (left) and its simplified numbering scheme (right). Hydrogen atoms and minor disordered part of the solvent DCM are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1−Ag2 = 3.0410(3), Ag1---Ag2b = 4.0607(3), Ag1---Ag2a = 5.9371(3), Ag1−O = 2.345(2)-2.394(2); Ag2−O = 2.321(2)-2.509(2), Ag1---O33 = 2.621(2), Ag1−Cl1 = 2.9042(9), Ag1−Ag2−Ag1a = 113.71(1), Ag2−Ag1−Ag2b = 102.17(1), Ag2−Ag1−Ag2b−Ag1b = 6.86(2).

$PyPPh_2$ ligand for the role of the hard nitrogen donor site to activate water, as is illustrated in Figure 7.[10a,11a,h] We opted for

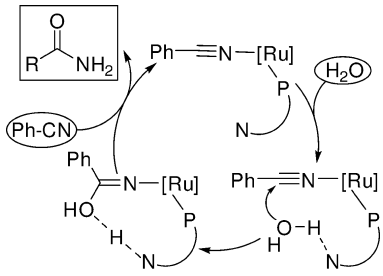


Figure 7. Ru-catalyzed, P,N-assisted hydration of benzonitrile.

ruthenium catalysts,[29] which are extensively used in homogeneous catalysis[30] and are more robust than those based on rhodium (for comparison and completeness also included in our tests), while their chemistry is comparable. This choice is corroborated by the elevated temperatures needed.

To identify a suitable Ru source for benchmarking iminophosphane **3a** against $PyPPh_2$ in the hydration of benzonitrile, we conducted the catalytic reactions in 1,2-dimethoxyethane, in water, and in the absence of a solvent. Table 1 gives the precatalyst, ligand, solvent, and the yield of benzamide. For the reactions in DME, the procedure of Takai, Oshiki, and co-workers[11h] was followed by premixing 5 mol % of the Ru precursor complex and **3a** for 30 min, upon which the catalyzed hydration of benzonitrile was executed in a closed vessel at 180 °C for 3 h; 2 equiv of water was used to remain consistent with the reported protocol. The results show that precatalyst $[Ru(p\text{-cymene})Cl_2]_2$ (entries 1 and 2) gives better results than $[Ru(C_6Me_6)Cl_2]_2$ (entry 5) and $[Ru(C_6H_5Me)Cl_2]_2$ (entry 6), but even these give reasonable conversions.

The presence of 1 equiv of AgOTf hindered the reaction (Table 1, entry 3), presumably through the formation of inactive bidentate species. Remarkable is the observation that the catalytic hydration using **3a** gave an excellent yield of 87% (entry 1), while the same process with the $PyPPh_2$ ligand performed very poorly with a product yield of a mere 3%[11h] (entry 4). Using 2 equiv of **3a** further enhanced the yield to 96% (entry 2). In addition, rhodium precatalyst $[RhCp^*Cl_2]_2$ was examined under the same conditions. Even this in situ generated catalyst, presumably **4a**, yields benzamide, albeit in only in 22% yield (entry 7), which is a remarkable observation,

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Table 1. Ru(II)-Catalyzed Hydration of Benzonitrile

entry	precatalyst (M)	ligand (L)	solvent	T (°C)	t (h)	yield[a] (%)
1[b]	$[Ru(p\text{-cym})Cl_2]_2$	**3a**	DME	180	3	87
2[b]	$[Ru(p\text{-cym})Cl_2]_2$	**3a**[c]	DME	180	3	96
3[b]	$[Ru(p\text{-cym})(Cl)\ (OTf)]_2$[d]	**3a**[d]	DME	180	3	3
4[b]	$[Ru(p\text{-cym})Cl_2]_2$	Ph_2PPy	DME	180	3	3[11h]
5[b]	$[Ru(C_6Me_6)Cl_2]_2$	**3a**	DME	180	3	55
6[b]	$[Ru(C_6H_5Me)Cl_2]_2$	**3a**	DME	180	3	84
7[b]	$[RhCp^*Cl_2]_2$	**3a**	DME	180	3	22
8[e]	$[Ru(p\text{-cym})Cl_2]_2$	**3a**	H_2O	100	24	94
9[e]	$[Ru(p\text{-cym})Cl_2]_2$	Ph_2PPy	H_2O	100	24	57[11a]
10[f]	$[Ru(p\text{-cym})Cl_2]_2$	**3a**	none	180	3	78
11[f]	$[Ru(p\text{-cym})Cl_2]_2$	Ph_2PPy	none	180	3	6
12[f]	$[Ru(p\text{-cym})Cl_2]_2$	none	none	180	3	6

[a]Determined by GC. [b]Conditions: Ph−C≡N (1 mmol), H_2O (2 mmol), [M]L (5 mol %); DME (0.5 mL). [c]2 equiv. [d]Prepared in situ from $[Ru(p\text{-cym})Cl_2]_2$ and AgOTf. [e]Conditions: Ph−C≡N (1 mmol), [M]L (5 mol %); H_2O (3.0 mL). [f]Conditions: Ph−C≡N (3.6 mmol), H_2O (7.2 mmol), [M]L (1.4 mol %).

as no Rh(III) catalyst has so far been reported to hydrate nitriles.

Next, we explored the protocol of Cadierno et al. by heating benzonitrile and 5 mol % of precatalyst $[Ru(p\text{-cym})Cl_2]_2$ and the 1,3-P,N ligand in boiling water for 24 h using a closed vessel.[11a,31] Also in this case an outstanding yield of 94% was obtained for the catalytic reaction with **3a** (Table 1, entry 8), which is far better than the 57% that resulted with the $PyPPh_2$ ligand (entry 9).[11a] This performance is in line with that with DME as solvent (entries 1 and 4) by also showing that the catalytic reaction with ligand **3a** outperforms that with Ph_2PPy. Finally, we compared the influence of these ligands in the solvent-free hydration of benzonitrile by heating 1.4 mol % of the catalyst in a 1:2 molar mixture of benzonitrile and water at 180 °C for 3 h in a closed vessel. Again, the reaction of $[Ru(p\text{-cym})Cl_2]_2$ and **3a** (78%, entry 10) gave a far better performance than that with the Ph_2PPy ligand (6%, entry 11), which, in fact, seems to have no effect, as 6% was also obtained when no P,N ligand was present (entry 12). It appears that all three Ru-catalyzed approaches for the hydration of benzonitrile underscore the potential of iminophosphanes as ligands. The observed differences in the activity of **3a** and $PyPPh_2$ were attributed to their difference in N-donor strength.[10a]

Finally, we address briefly the influence of the P,C,N substituents of **3** on the yield of the Ru(II)-catalyzed hydration using solvent-free conditions. The results are given in Table 2.

Whereas the iminophosphanes are only modestly different from each other, some distinctly affected the benzamide yield. As a reference we used **3a**, which has Ph substituents on the P and C centers and a Me group on the N atom. The catalyzed hydration yield of benzonitrile amounted to 78% (Table 2, entry 1). Changing the N substituent from Me to the bulkier *i*-Pr group (**3g**) decreased the yield by only 3% (entry 5). A similar marginal effect (−2%) was observed on introducing a 4-CF_3 substituent on the *C*-phenyl group (**3c**, entry 2). Slightly larger effects were found on introducing 3-CH_3 and 3-CF_3 substituents on the *P*-phenyl groups, causing modest changes in yield of +4% (entry 3) and −8% (entry 4), respectively. These may possibly be attributed to a difference in electron-donating properties, which affect ruthenium's Lewis acidity via the Ru−P bond.[14d] All of this leads to the observation that the iminophosphanes **3** are all effective ligands enabling the solvent-free Ru(II)-catalyzed hydration of benzonitrile and that these 1,3-P,N ligands can be modified at the P, C, and N centers to effect the hydration to different degrees.

Table 2. Solvent-Free [(3)Ru(*p*-cym)Cl_2]-Catalyzed Hydration of Benzonitrile[a]

entry	ligand (L)	solvent	T (°C)	t (h)	yield[b] (%)
1	**3a**	none	180	3	78
2	**3c**	none	180	3	76
3	**3d**	none	180	3	82
4	**3e**	none	180	3	70
5	**3g**	none	180	3	75

[a]Conditions: Ph−C≡N (3.6 mmol), H_2O (7.2 mmol), $[Ru(p\text{-cym})Cl_2]$L (1.4 mol %). [b]Determined by GC.

CONCLUSION

This study shows iminophosphanes to be readily synthesized by simple alkylation of nitriles and reaction of the resulting nitrilium ions with a secondary phosphane. They are very stable in water but do show some sensitivity to oxidation in air. The 1,3-P,N ligands are tunable by substitution at their P, C, and N centers. Their coordination behavior was explored for rhodium(III) complexes, using $[RhCp^*Cl_2]_2$ as precursor. Both P monodentate and 1,3-P,N bidentate ligands can be obtained in high yield. Silver triflate is needed to enforce the formation of the κ^2 chelates, and when an excess is used, also the second chloride is exchanged. Several X-ray crystal structures of rhodium complexes are reported, including one with a polymeric aggregate of Ag(I) sulfonate with embedded DCM solvent molecules. The ligands were found to be effective in the Ru(II)-catalyzed hydration of benzonitrile, be it in an organic solvent, in water, or under solvent-free conditions. Its performance appears to be better than that of 2-pyridyldiphenylphosphane, with yields of up to 96% on using the commercial $[Ru(p\text{-cym})Cl_2]_2$ as precatalyst. Modifying the substitution pattern of the iminophosphanes affects the yield of the ruthenium-catalyzed hydration of benzonitrile as well as the coordination to the rhodium complex. Clearly, more extensive studies have to be performed for more catalytic processes, but the easily synthesized iminophosphanes seem to have great prospects as new 1,3-P,N ligands.

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EXPERIMENTAL SECTION

Preparation of Compounds. All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk-line and glovebox techniques, unless stated otherwise. Solvents were distilled under nitrogen over the appropriate drying agent; $CaCl_2$ (DCM), benzophenone/NaK (Et_2O, THF, triethylamine), Na (toluene), $LiAlH_4$ (pentane), P_2O_5 (CD_2Cl_2, $CDCl_3$). C_6D_6 was dried over Na at room temperature. H_2O was degassed ultrasonically in vacuo. Silver salts were handled with minimum light exposure. Diphenylphosphane was purchased from Sigma-Aldrich, and tris(3-methylphenyl)-phosphane and bis(4-methylphenyl)chlorophosphane were obtained from STREM Chemicals Inc. Bis(3-trifluoromethylphenyl)-chlorophosphane was provided by Arkema B.V. The known compounds **2a**,[22b] bis(3-trifluoromethylphenyl)phosphane, bis(3-methylphenyl)phosphane, and bis(4-methylphenyl)phosphane are reported here, since their syntheses were revised and/or new analytical data were obtained. All phosphanes and chlorophosphanes were distilled under reduced pressure before use. Solids were predried in vacuo for at least 30 min. All other reagents were used as received. NMR spectra were recorded on a Bruker Avance 250 (^{1}H, 250.13 MHz; ^{19}F, 235.36 MHz; ^{31}P, 101.25 MHz; room temperature), a Bruker Avance 400 (^{1}H, 400.13 MHz; ^{13}C{^{1}H}, 100.61 MHz; ^{31}P, 161.98 MHz; room temperature) ,or a Bruker Avance 500 instrument (^{1}H, 500.23 MHz; ^{13}C{^{1}H}, 125.78 MHz; room temperature). ^{1}H spectra and ^{13}C{^{1}H} spectra were internally referenced to residual solvent resonances ($CDCl_3$, $\delta(^1H)$ 7.26, $\delta(^{13}C\{^1H\})$ 77.16; CD_2Cl_2, $\delta(^1H)$ 5.32, $\delta(^{13}C\{^1H\})$ 53.84; C_6D_6, $\delta(^1H)$ 7.16, $\delta(^{13}C\{^1H\})$ 128.06), and ^{31}P spectra were referenced externally to H_3PO_4. Melting points were measured using a Büchi M-565 melting point apparatus (sealed capillaries) and are uncorrected. High-resolution electrospray ionization (ESI) mass spectrometry was carried out with a Bruker micrOTOF-Q instrument in positive ion mode (capillary potential of 4500 V). Infrared spectra were recorded on a Shimadzu FT-IR 8400S spectrophotometer.

Computational Procedure. Density functional calculations were performed at the ωB97X-D[32] level of theory using Gaussian09, revision A.02.[23] Geometry optimizations were performed using the 6-31+G(d,p)[33] basis set (Def2-TZVP for Rh),[34] and the nature of each stationary point was confirmed by frequency calculations.

(*N*-Methyl)(aryl)carbonitrilium Trifluoromethyl Sulfonates 2a–c.[22b] *Protocol 1.* MeOTf (1.0 equiv) was added dropwise to a solution of arylnitrile (1.0 equiv) in toluene (0.27 mL/mmol of arylnitrile). After the mixture was stirred for 18 h at room temperature, a microcrystalline solid precipitated. Volatiles were removed in vacuo, and after washing with pentane (2 × 0.4 mL/mmol), **2** was obtained as an off-white solid (**2a**, 62%; **2b**, 62%; **2c**: 14%).

Protocol 2. MeOTf (1.0 equiv) was added dropwise to the arylnitrile (1.2 equiv). The colorless solution was stirred for 18 h (**2a**, room temperature; **2c**, 45 °C). The resulting white-yellow crystalline solid was washed with pentane (3 × 0.2 mL/mmol) and dried in vacuo to provide **2** as a white solid (**2a**, 86%; **2c**, 69%).

Crystallization was carried out by slow 1:1 diffusion of ether (alternatively pentane) into a saturated DCM solution at 5 °C to provide **2** as white crystals.

Data for **2a** are as follows. Mp: 78.9–79.9 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 8.31 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; *o*-PhH), 7.92 (t, $^3J_{H,H}$ = 7.8 Hz, 1H; *p*-PhH), 7.65 (t, $^3J_{H,H}$ = 8.0 Hz, 2H; *m*-PhH), 4.20 (s, 3H; NCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 138.6 (s; *p*-PhC), 136.2 (s; *m*-PhC), 130.1 (s; *o*-PhC), 120.9 (q, $^1J_{C,F}$ = 319.5 Hz; O_3SCF_3), 106.8 (tm, $^1J_{C,14N}$ = 47.2 Hz; CN), 103.0 (s; *ipso*-PhC), 32.6 (s; NCH_3). ^{19}F{^{1}H} NMR (235.36 MHz, $CDCl_3$): δ −78.3 (s; O_3SCF_3). FT-IR (cm^{-1}): ν 3277 (w), 3248 (w), 3186 (w), 3026 (w), 2957 (w), 2457 (w), 2366 (s), 1680 (m), 1583 (m), 1528 (m), 1489 (w), 1448 (m), 1402 (m), 1371 (m), 1261 (s), 1223 (s), 1180 (s), 1148 (s), 1024 (s), 987 (s), 943 (m), 843 (w), 762 (s), 704 (s), 679 (s), 633 (s), 573 (s), 538 (s), 515 (s), 484 (w), 467 (m), 426 (w), 413 (w). MS (ESI-Q-TOF): calcd for C_8H_8N: 118.0651; found 118.0657.

Data for **2b** are as follows. Mp: 117.0 °C dec; 135.1–135.8 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 8.18 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; *o*-ArH), 7.45 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; *m*-ArH), 4.18 (s, 3H; NCH_3), 2.51 (s, 3H; $C_6H_4CH_3$). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 151.3 (s; *p*-ArC), 136.1 (s; *o*-ArC), 131.1 (s; *m*-ArC), 120.9 (q, $^1J_{C,F}$ = 319.5 Hz; O_3SCF_3), 107.7 (tm, $^1J_{C,14N}$ = 50.9 Hz; CN), 99.4 (s; *ipso*-ArC), 32.5 (s; NCH_3), 22.9 (s; $C_6H_4CH_3$). ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −78.4 (s, O_3SCF_3). FT-IR (cm^{-1}): ν 3051 (w), 2959 (w), 2473 (w), 2424 (w), 2368 (s), 2328 (w), 1670 (w), 1605 (s), 1506 (w), 1418 (m), 1389 (m), 1258 (s), 1225 (s), 1192 (s), 1148 (s), 1128 (s), 1028 (s), 974 (w), 943 (s), 824 (s), 791 (m), 756 (s), 739 (m), 702 (w), 635 (s), 573 (s), 540 (s), 517 (s), 488 (w), 447 (m), 438 (m), 409 (w). MS (ESI-Q-TOF): calcd for $C_9H_{10}N$ 132.0808; found 132.0811.

Data for **2c** are as follows. Mp: 106.9–108.0 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 8.50 (d, $^3J_{H,H}$ = 8.3 Hz, 2H; *o*-ArH), 7.90 (d, $^3J_{H,H}$ = 8.3 Hz, 2H; *m*-ArH), 4.26 (s, 3H; NCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 162.5 (d, $^2J_{C,F}$ = 13.8 Hz; *p*-ArC), 139.4 (q, $^1J_{C,F}$ = 34.0 Hz; $C_6H_4CF_3$), 137.1 (s; *o*-ArC), 127.0 (s; *m*-ArC), 122.4 (q, $^1J_{C,F}$ = 274.2 Hz; O_3SCF_3), 107.4 (s; *ipso*-ArC), 105.2 (tm, $^1J_{C,14N}$ = 50.0 Hz; CN), 32.9 (s; NCH_3). ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −64.5 (s; $C_6H_4CF_3$), −78.7 (s; O_3SCF_3). FT-IR (cm^{-1}): ν 3117 (w), 3067 (w), 3036 (w), 2957 (w), 2366 (s), 1688 (w), 1508 (w), 1412 (m), 1389 (w), 1319 (s), 1252 (s), 1225 (s), 1165 (s), 1130 (s), 1113 (s), 1067 (s), 1030 (s), 1018 (s), 928 (w), 847 (s), 756 (s), 733 (w), 706 (s), 683 (w), 636 (s), 596 (s), 573 (s), 536 (s), 517 (s), 469 (m), 449 (m), 432 (m). MS (ESI-Q-TOF): calcd for $C_9F_3H_7N$ 186.0525; found 186.0533.

Bis(3-trifluoromethylphenyl)phosphane.[35] A solution of freshly distilled bis(3-trifluoromethylphenyl)chlorophosphane (5.88 g, 16.50 mmol, 1.00 equiv) in 30 mL of Et_2O was added dropwise at −78 °C to a suspension of $LiAlH_4$ (0.25 g, 6.59 mmol, 0.40 equiv) in 50 mL of Et_2O, during which gas evolved from the mixture. After addition, the gray suspension was warmed to room temperature. After it was stirred for 1.5 h, the mixture was cooled to 0 °C and H_2O (0.95 mL, 52.63 mmol, 3.19 equiv) was added dropwise. After the mixture was stirred for 0.5 h at room temperature, volatiles were removed in vacuo and the resulting gray-white suspension was extracted into 3 × 10 mL of pentane. The combined extracts were evaporated to provide bis(3-trifluoromethylphenyl)phosphane as a colorless liquid (4.94 g, 15.33 mmol, 93%). ^{1}H NMR (500.23 MHz, C_6D_6): δ 7.61 (d, $^3J_{H,P}$ = 6.9 Hz, 2H; PC−CH-CCF$_3$), 7.17 (d, $^3J_{H,H}$ = 6.3 Hz, 2H; *p*-ArH), 7.05 (t, $^3J_{H,H}$ = 6.9 Hz, 2H; PC−CH-CH), 6.71 (t, $^3J_{H,H}$ = 7.7 Hz, 2H; *m*-ArH), 4.81 (d, $^1J_{H,P}$ = 219.7 Hz, 1H; PH). ^{13}C{^{1}H} NMR (125.78 MHz, C_6D_6): δ 137.2 (d, $^2J_{C,P}$ = 17.3 Hz; PC−CH-CH), 135.9 (d, $^1J_{C,P}$ = 13.6 Hz; *ipso*-ArC), 131.2 (qd, $^2J_{C,F}$ = 32.7 Hz, $^3J_{C,P}$ = 6.4 Hz; PC-CH-CCF$_3$), 130.5 (dq, $^2J_{C,P}$ = 18.2 Hz, $^3J_{C,F}$ = 4.5 Hz; PC-CH-CCF$_3$), 129.3 (d, $^3J_{C,P}$ = 5.5 Hz; *m*-ArC), 125.7 (q, $^3J_{C,F}$ = 3.6 Hz; *p*-ArC), 124.6 (q, $^1J_{C,F}$ = 272.5 Hz; CF_3). ^{19}F NMR (235.36 MHz, C_6D_6): δ −63.3 (s; $C_6H_4CF_3$). ^{31}P NMR (161.98 MHz, C_6D_6): δ −41.1 (dq, $^1J_{P,H}$ = 218.3 Hz, $^3J_{P,H}$ = 6.7 Hz).

Bis(3-methylphenyl)phosphane.[36] A colorless solution of tris(3-methylphenyl)phosphane (4.18 g, 13.73 mmol, 1.00 equiv) in 30 mL of THF was prepared in a separate vessel and added dropwise at 0 °C to an excess of finely cut Li (0.21 g 30.23 mmol, 2.20 equiv) suspended in 5 mL of THF. Afterward, the vessel was washed with 2 × 10 mL of THF, which was also added to the reaction mixture. After addition, the mixture was warmed to room temperature. After this mixture was stirred for 26 h at room temperature, a deep red mixture was obtained, which was decanted to remove excess Li. The resulting solution was cooled to 0 °C, and H_2O (1.0 mL, 55.40 mmol, 4.04 equiv) was added dropwise to give a white-gray mixture. After 1 h of stirring at room temperature, volatiles were removed in vacuo to provide a white oil, which was extracted sequentially into 50 mL of Et_2O for 24 h and 40 mL of Et_2O for 20 h. The combined extracts were evaporated to give a light yellow liquid, which was distilled (3.2 × 10^{-2} mbar, heated with Bunsen burner) to provide bis(3-methylphenyl)phosphane (1.71 g, 7.99 mmol, 58%) as a colorless liquid. ^{1}H NMR (500.23 MHz, C_6D_6): δ 7.30 (t, $^3J_{H,H}$ = 8.2 Hz, 4H; *o*-ArH), 7.00 (t, $^3J_{H,H}$ = 7.4 Hz, 2H; *m*-ArH), 6.87 (d, $^3J_{H,H}$ = 6.6 Hz, 2H; *p*-ArH), 5.27 (d, $^1J_{H,P}$ = 215.0 Hz, 1H; PH), 1.99 (s, 6H; CH_3). ^{13}C{^{1}H} NMR (125.78 MHz, C_6D_6): δ 138.3 (d, $^2J_{C,P}$ = 6.4 Hz; *m*-ArC-CH_3), 135.4 (d, $^1J_{C,P}$ = 10.9 Hz; *ipso*-ArC), 135.0 (d, $^2J_{C,P}$ = 18.2

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Hz; *o*-ArC), 131.5 (d, $^2J_{C,P}$ = 16.4 Hz; *o*-ArC), 129.5 (s; *p*-ArC), 128.8 (d, $^3J_{C,P}$ = 6.4 Hz; *m*-ArC), 21.2 (s; CH_3). ^{31}P NMR (161.98 MHz, C_6D_6): δ −40.3 (dq, $^1J_{P,H}$ = 215.4 Hz, $^3J_{P,H}$ = 7.9 Hz).

Bis(4-methylphenyl)phosphane.[35] A solution of bis(4-methylphenyl)chlorophosphane (1.81 mL, 8.01 mmol, 1.00 equiv) in 15 mL of Et_2O was added dropwise to a suspension of $LiAlH_4$ (0.094 g 2.48 mmol, 0.31 equiv) at −78 °C. After addition, the gray suspension was warmed to room temperature. After it was stirred for 1.5 h at room temperature, the mixture was cooled to 0 °C and H_2O (0.15 mL, 8.31 mmol, 1.04 equiv) was added dropwise. After it was stirred for 1 h at room temperature, the gray-white suspension was filtered onto anhydrous Na_2SO_4 (2.71 g), after which it was filtered again. Volatiles were removed in vacuo to provide a white suspension, which was extracted into 20 mL of pentane. After evaporation of the extract, the obtained white suspension was distilled (2.3×10^{-2} mbar, 100 °C). Bis(4-methylphenyl)phosphane (0.81 g, 3.78 mmol, 47%) was obtained as a colorless liquid. ^{1}H NMR (500.23 MHz, C_6D_6): δ 7.38 (t, $^3J_{H,H}$ = 7.8 Hz, 4H; *o*-ArH), 6.89 (d, $^3J_{H,H}$ = 7.5 Hz, 4H; *m*-ArH), 5.28 (d, $^1J_{H,P}$ = 214.1 Hz, 1H; PH), 2.02 (s, 6H; CH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 138.4 (s; *p*-ArC), 134.5 (d, $^2J_{C,P}$ = 17.3 Hz; *o*-ArC), 132.2 (d, $^2J_{C,P}$ = 9.1 Hz; *ipso*-ArC), 129.7 (d, $^3J_{C,P}$ = 6.4 Hz; *m*-ArC), 21.1 (s; CH_3). ^{31}P NMR (161.98 MHz, C_6D_6): δ −42.6 (dq, $^1J_{P,H}$ = 215.4 Hz, $^3J_{P,H}$ = 3.2 Hz).

((*N*-Methyl)arylimidoyl)diarylphosphanes 3a−f. ***Protocol 3a−d.*** Diarylphosphane (1.0 equiv) was added dropwise to a solution of **2a** (1.1 equiv) in DCM (4.0 mL/mmol) at −78 °C to give a bright yellow solution, which was warmed to room temperature and stirred for 15 min. Triethylamine (1.1 equiv) was added to give a yellow solution, which was stirred for 1 h. Volatiles were removed in vacuo to give a yellow oil, which was extracted into Et_2O (3 × 4 mL/mmol). The extract was concentrated to saturation and filtered over neutral alumina. Evaporation provided **3** as an off-white solid (mixture of *E* and *Z* isomers; **3a** 91%, **3b** 75%, **3c** 85%, **3d** 45%*) (*for crystallization, a saturated Et_2O solution was cooled to −80 °C).

Protocol 3e,f. Diarylphosphane (1.0 equiv) was added dropwise to a solution of **2a** (1.1 equiv) in DCM (4.0 mL/mmol) at −78 °C to give a bright yellow solution, which was warmed to room temperature and stirred for 15 min. Triethylamine (1.1 equiv) was added to give a yellow solution, which was stirred for 1 h. Volatiles were removed in vacuo to provide a yellow oil, which was extracted into Et_2O overnight (3 × 4 mL/mmol). The extract was concentrated to saturation and filtered over neutral alumina. Evaporation provided an off-white solid, which was extracted into pentane (5 mL/mmol). Evaporation of the extract provided **3e−f** (**3e** 77%*, **3f** 53%) (*for crystallization, a saturated pentane solution was cooled to −80 °C).

Data for **3a** are as follows. Mp: 79.0−79.4 °C. *Since not all ^{1}H and ^{13}C NMR resonances of E-**3a** and Z-**3a** can be distinguished, one set of signals is reported (integrals normalized separately for each isomer).* ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.45−7.38 (m, 4H; P-ArH (*E*)), 7.32−7.21 (m, 6H; P-ArH (*E*) and 10H; ArH (*Z*)), 7.21−7.13 (m, 3H; C-*m,p*-ArH (*E*)), 7.09−7.03 (m, 1H; ArH (*Z*)), 7.03−6.99 (m, 4H; C-ArH (*Z*)), 6.95 (d, $^3J_{H,H}$ = 6.6 Hz, 2H; C-*o*-ArH (*E*)), 3.57 (s, 3H; CN-CH_3 (*Z*)), 3.25 (d, $^4J_{H,P}$ = 0.9 Hz, 3H; CN-CH_3 (*E*)). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 179.2 (d, $^1J_{C,P}$ = 8.2 Hz; *C*N-CH_3 (*E*)), 176.7 (d, $^1J_{C,P}$ = 42.7 Hz; *C*N-CH_3 (*Z*)), 141.4 (d, $^2J_{C,P}$ = 7.3 Hz, C-*ipso*-ArC (*Z*)), 137.6 (d, $^2J_{C,P}$ = 24.5 Hz; C-*ipso*-ArC (*E*)), 134.7 (d, $J_{C,P}$ = 19.1 Hz, P-ArC (*E*)), 134.6 (d, $^1J_{C,P}$ = 10.0 Hz; P-*ipso*-ArC (*Z*)), 133.9 (d, $J_{C,P}$ = 20.0 Hz; P-ArC (*Z*)), 133.9 (s; P-*ipso*-ArC (*E*)), 129.1 (s; P-ArC (*Z*)), 129.0 (s; P-ArC (*E*)), 128.8 (s; P-ArC (*Z*)), 128.7 (d, $J_{C,P}$ = 7.3 Hz; C-ArC (*E*)), 128.5 (d, $J_{C,P}$ = 20.9 Hz; P-ArC (*E*)), 128.3 (d, $^5J_{C,P}$ = 7.3 Hz; C-ArC (*Z*), 128.2 (s; C-ArC (*E*)), 128.0 (d, $^4J_{C,P}$ = 20.0 Hz; C-ArC (*Z*)), 127.6 (d, $^3J_{C,P}$ = 5.4 Hz; C-ArC (*Z*)), 127.0 (d, $^3J_{C,P}$ = 3.6 Hz; C-*o*-ArC (*E*)), 43.9 (d, $^3J_{C,P}$ = 33.6 Hz; CN-CH_3 (*Z*)), 43.2 (d, $^3J_{C,P}$ = 8.2 Hz; CN-CH_3 (*E*)). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 7.8 (t, $^3J_{P,H}$ = 7.9 Hz; *E* isomer, 71%); −7.6 (t, $^3J_{P,H}$ = 7.9 Hz; *Z* isomer, 29%). FT-IR (cm^{-1}): ν 3069 (m), 2901 (m), 2849 (w), 2746 (w), 1599 (s), 1572 (w), 1518 (w), 1479 (s), 1433 (s), 1383 (m), 1367 (w), 1277 (m), 1261 (m), 1242 (m), 1202 (m), 1155 (m), 1090 (m), 1067 (m), 1028 (s), 974 (m), 939 (m), 903 (m), 862 (m), 839 (m), 808 (m), 758 (s), 737 (s), 692 (s), 640 (s), 609 (s), 573 (s), 548 (m), 507 (s), 474 (s), 449 (s), 426 (s). HR-MS (ESI-Q-TOF): calcd for $C_{20}H_{19}NP$ 304.1250; found 304.1245.

Data for **3b** are as follows. Mp: 44.0−46.1 °C. *Since not all ^{1}H and ^{13}C NMR resonances of E-**3b** and Z-**3b** can be distinguished, one set of signals is reported (integrals normalized separately for each isomer).* ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.46−7.39 (m, 6H; P-ArH (*E*), P-ArH (*Z*)), 7.32−7.23 (m, 14H; P-ArH (*E*), P-ArH (*Z*)), 7.02 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; C-*o*-ArH (*E*)), 6.95 (d, $^3J_{H,H}$ = 8.2 Hz, 2H; C-*o*-ArH (*Z*)), 6.89 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; C-*m*-ArH (*E*)), 6.84 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; C-*m*-ArH (*Z*)), 3.56 (s, 3H; CN-CH_3 (*Z*), 3.26 (d, $^4J_{H,P}$ = 1.9 Hz, 3H; CN-CH_3 (*E*)), 2.26 (s, 3H; C-Ar-CH_3 (*E*)), 2.20 (s, 3H; C-Ar-CH_3 (*Z*)). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 179.1 (d, $^1J_{C,P}$ = 8.2 Hz; CN-CH_3 (*E*)), 139.4 (s; C-*ipso*-ArC (*Z*)), 138.0 (s; C-*ipso*-ArC (*E*)), 134.8 (d, $J_{C,P}$ = 20.0 Hz; P-ArC (*E*)), 134.8 (s; P-*ipso*-ArC (*Z*)), 134.6 (d, $^1J_{C,P}$ = 10.9 Hz; P-*ipso*-ArC (*E*)), 133.9 (d, $J_{C,P}$ = 19.1 Hz; P-ArC (*Z*)), 129.0 (s; P-ArC (*E*)), 129.0 (s; P-ArC (*Z*)), 128.9 (s; P-ArC), 128.8 (d, $J_{C,P}$ = 7.3 Hz; P-ArC), 128.3 (d, $^4J_{C,P}$ = 10.3 Hz; C-*m*-ArC (*Z*)), 127.8 (s; C-*o*-ArC (*Z*)), 127.1 (d, $^4J_{C,P}$ = 4.1 Hz; C-*m*-ArC (*E*)), 43.6 (d, $^3J_{C,P}$ = 36.3 Hz; CN-CH_3 (*Z*)), 43.2 (d, $^3J_{C,P}$ = 9.1 Hz; CN-CH_3 (*E*)), 21.4 (s; C-Ar-CH_3 (*E*)), 21.3 (s; C-Ar-CH_3 (*Z*)). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 7.6 (s; *E* isomer, 83%), −8.0 (s; *Z* isomer, 17%). FT-IR (cm^{-1}): ν 3072 (m), 3001 (m), 2943 (m), 2907 (m), 2853 (m), 2756 (m), 1601 (s), 1570 (m), 1506 (s), 1481 (s), 1433 (s), 1404 (m), 1391 (s), 1375 (m), 1310 (m), 1261 (m), 1217 (m), 1182 (s), 1157 (m), 1111 (s), 1095 (s), 1065 (s), 1028 (s), 970 (s), 951 (s), 920 (s), 845 (m), 812 (s), 791 (s), 733 (s), 690 (s), 665 (s), 635 (s), 619 (s), 525 (s), 484 (s), 453 (s), 440 (s), 411 (s). HR-MS (ESI-Q-TOF): calcd for $C_{21}H_{21}NP$ 318.1406; found 318.1404.

Data for **3c** are as follows. Mp: 46.8−47.4 °C. *Since not all ^{1}H and ^{13}C NMR resonances of E-**3c** and Z-**3c** can be distinguished, one set of signals is reported (integrals normalized separately for each isomer).* ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.47−7.38 (m, 6H; P-ArH (*E*), P-ArH (*Z*), C-ArH (*E*)), 7.33−7.22 (m, 18H; P-ArH (*E*), P-ArH (*Z*), C-ArH (*Z*)), 7.11 (d, $^3J_{H,H}$ = 8.2 Hz, 2H; C-ArH (*Z*)), 7.04 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; C-ArH (*E*)), 3.60 (s; CN-CH_3 (*Z*)), 3.24 (d, $^4J_{H,P}$ = 1.6 Hz; CN-CH_3 (*E*)). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 178.0 (d, $^1J_{C,P}$ = 9.1 Hz; *C*N-CH_3), 144.6 (d, $^2J_{C,P}$ = 6.4 Hz; C-*ipso*-ArC), 141.3 (d, $^2J_{C,P}$ = 24.5 Hz; C-*ipso*-ArC), 134.7 (d, $J_{C,P}$ = 20.0 Hz, P-ArC), 133.8 (d, $J_{C,P}$ = 19.1 Hz; P-ArC), 133.8 (d, $^1J_{C,P}$ = 9.1 Hz; P-*ipso*-ArC), 133.2 (d, $^1J_{C,P}$ = 9.1 Hz; P-*ipso*-ArC), 130.2 (q, $^1J_{C,F}$ = 31.8 Hz; CF_3), 129.4 (d, $J_{C,P}$ = 8.2 Hz; P-ArC), 129.0 (d, $J_{C,P}$ = 7.3 Hz; P-ArC), 128.5 (d, $J_{C,P}$ = 7.3 Hz; P-ArC), 128.0 (s; C-ArC (*Z*)), 127.4 (d, $J_{C,F}$ = 3.6 Hz; C-ArC (*E*)), 125.2 (q, $J_{C,F}$ = 3.6 Hz; C-ArC (*E*)), 125.1 (d, $^2J_{C,F}$ = 14.5 Hz; C-*p*-ArC), 124.5 (q, $J_{C,F}$ = 7.7 Hz; C-ArC (*Z*)), 123.0 (d, $^2J_{C,F}$ = 14.5 Hz; C-*p*-ArC), 44.1 (d, $^3J_{C,P}$ = 32.7 Hz; CN-CH_3 (*Z*)), 43.4 (d, $^3J_{C,P}$ = 8.2 Hz; CN-CH_3 (*E*)). ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −62.7 (s; *Z* isomer, 55%), −62.8 (s; *E* isomer, 45%). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 8.2 (t, $^3J_{P,H}$ = 6.7 Hz; *E* isomer, 45%), −7.7 (s; *Z* isomer, 55%). FT-IR (cm^{-1}): ν 3074 (w), 3065 (w), 3051 (w), 2962 (w), 2932 (w), 1664 (w), 1610 (w), 1582 (m), 1568 (m), 1483 (m), 1435 (m), 1406 (m), 1385 (m), 1321 (s), 1261 (m), 1236 (w), 1157 (s), 1109 (s), 1065 (s), 1009 (s), 999 (s), 970 (m), 918 (m), 843 (s), 818 (m), 802 (m), 771 (m), 743 (s), 696 (s), 681 (s), 650 (s), 615 (s), 598 (m), 579 (w), 546 (m), 507 (s), 482 (s), 447 (s), 430 (m), 419 (m). HR-MS (ESI-Q-TOF): calcd for $C_{21}F_3H_{18}NP$ 372.1123; found 372.1123.

Data for **3d** are as follows. Mp: 40.6 °C dec. *Since not all ^{1}H and ^{13}C NMR resonances of E-**3d** and Z-**3d** can be distinguished, one set of signals is reported (integrals normalized separately for each isomer).* ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.71 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; ArH (*E*)), 7.68−7.54 (m, 9H; ArH (*E*), ArH (*Z*)), 7.49−7.41 (m, 6H; ArH (*E*), ArH (*Z*)), 7.31−7.22 (m, 2H; ArH (*Z*)), 7.14 (t, $^3J_{H,H}$ = 7.9 Hz, 1H; ArH (*Z*)), 7.08 (t, $^3J_{H,H}$ = 7.6 Hz, 2H; ArH (*Z*)), 7.00 (d, $^3J_{H,H}$ = 7.3 Hz, 2H; ArH (*E*)), 6.97 (d, $^3J_{H,H}$ = 7.3 Hz, 2H; ArH (*Z*)), 3.65 (s, 3H; CN-CH_3 (*Z*)), 3.34 (s, 3H; CN-CH_3 (*E*)). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 177.5 (d, $^1J_{C,P}$ = 8.2 Hz; *C*N-CH_3 (*E*)), 171.8 (s; CN-CH_3 (*Z*)), 140.3 (d, $^2J_{C,P}$ = 8.2 Hz; C-*ipso*-ArC), 137.8 (d, $J_{C,P}$ = 19.1 Hz; ArC), 137.2 (t, $J_{C,P}$ = 10.9 Hz; ArC), 136.8 (d, $J_{C,P}$ = 15.4 Hz; ArC), 136.6 (d, $^2J_{C,P}$ = 25.4 Hz, C-*ipso*-ArC), 135.5 (d, $^1J_{C,P}$ = 12.3 Hz; P-*ipso*-ArC), 134.9 (d, $^1J_{C,P}$ = 12.7 Hz; P-*ipso*-ArC), 131.5 (q, $J_{C,F}$ = 3.6

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Hz; P-ArC (*E*)), 131.3 (q, $J_{C,F}$ = 3.6 Hz; P-ArC (*E*)), 131.2−130.3 (m; P-ArC-CF_3, P-ArC), 129.4 (s; ArC), 129.4 (t, $J_{C,P}$ = 2.7 Hz; ArC), 128.9 (d, $J_{C,P}$ = 7.3 Hz; ArC), 128.7 (s; ArC), 128.6 (s; ArC (*Z*)), 127.9 (s; ArC), 127.3 (s; ArC), 126.9 (d, $J_{C,P}$ = 4.5 Hz; ArC (*E*)), 126.5 (q, $J_{C,F}$ = 3.6 Hz; P-ArC (*Z*)), 126.2 (q, $J_{C,F}$ = 3.6 Hz; P-ArC (*E*)), 124.0 (q, $^1J_{C,F}$ = 272.5 Hz; CF_3 (*E*)), 123.8 (qd, $^1J_{C,F}$ = 272.5, $^4J_{C,P}$ = 5.4 Hz; CF_3 (*Z*)), 44.1 (d, $^3J_{C,P}$ = 34.5 Hz; CN-CH_3(*Z*)), 43.2 (d, $^3J_{C,P}$ = 8.2 Hz; CN-CH_3 (*E*)). ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −62.8 (s; *E* isomer, 62%), −62.9 (s; *Z* isomer, 38%). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 5.9 (t, $^3J_{P,H}$ = 6.5 Hz; *E* isomer, 83%), −8.5 (s; *Z* isomer, 17%). FT-IR (cm^{-1}): ν 3065 (w), 2962 (w), 1624 (m), 1603 (m), 1522 (m), 1479 (w), 1443 (m), 1416 (m), 1367 (w), 1321 (s), 1310 (s), 1259 (s), 1225 (m), 1161 (s), 1107 (s), 1088 (s), 1067 (s), 1028 (s), 999 (s), 935 (w), 905 (m), 891 (w), 866 (w), 795 (s), 762 (m), 743 (m), 692 (s), 683 (s), 636 (s), 611 (m), 575 (m), 542 (m), 517 (s), 482 (s), 467 (s), 453 (s). HR-MS (ESI-Q-TOF): calcd for $C_{22}F_6H_{17}NP$ 440.0997; found 440.1002.

Data for **3e** are as follows. Mp: n.a. (≤−20 °C). *Since not all ^{1}H and ^{13}C NMR resonances of E-**3e** and Z-**3e** can be distinguished, one set of signals is reported (integrals normalized separately for each isomer).* ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.25−7.12 (m, 13H; Ar*H*), 7.12−7.06 (m, 9H; Ar*H*), 7.06−7.00 (m, 4H; Ar*H*), 6.96 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; Ar*H* (*E*)), 3.58 (s, 3H; CN-CH_3 (*Z*)), 3.26 (s, 3H; CN-CH_3 (*E*)), 2.26 (s, 6H; P-Ar-CH_3 (*E*)), 2.24 (s, 6H; P-Ar-CH_3 (*Z*)). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 179.4 (d, $^1J_{C,P}$ = 7.3 Hz; *C*N-CH_3 (*E*)), 177.0 (d, $^1J_{C,P}$ = 42.7 Hz; *C*N-CH_3 (*Z*)), 141.5 (d, $^2J_{C,P}$ = 7.3 Hz; C-*ipso*-ArC (*Z*)), 138.3 (d, $^3J_{C,P}$ = 7.3 Hz; P-Ar*C*-CH_3), 137.8 (d, $^3J_{C,P}$ = 8.2 Hz; P-Ar*C*-CH_3), 137.8 (d, $^2J_{C,P}$ = 24.5 Hz; C-*ipso*-ArC (*E*)), 135.5 (d, $J_{C,P}$ = 20.9 Hz; ArC), 134.6 (d, $J_{C,P}$ = 21.8 Hz; ArC), 134.3 (d, $^1J_{C,P}$ = 9.1 Hz; P-*ipso*-ArC), 133.7 (d, $^1J_{C,P}$ = 9.1 Hz; P-*ipso*-ArC), 131.7 (d, $J_{C,P}$ = 17.3 Hz; ArC), 130.8 (d, $J_{C,P}$ = 17.3 Hz; ArC), 129.8 (d, $J_{C,P}$ = 20.9 Hz; ArC), 129.0 (d, $J_{C,P}$ = 39.1 Hz; ArC), 128.5 (d, $J_{C,P}$ = 7.3 Hz; ArC), 128.2 (d, $J_{C,P}$ = 7.3 Hz; ArC), 128.0 (d, $J_{C,P}$ = 19.1 Hz; ArC), 127.5 (d, $J_{C,P}$ = 22.7 Hz; ArC (*Z*)), 127.1 (s; ArC (*E*)), 127.0 (s; ArC (*E*)), 43.9 (d, $^3J_{C,P}$ = 33.6 Hz; CN-CH_3 (*Z*)), 43.3 (d, $^3J_{C,P}$ = 9.1 Hz; CN-CH_3 (*E*)), 21.6 (s; P-Ar-CH_3 (*E*)), 21.5 (s; P-Ar-CH_3 (*Z*)). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 8.3 (s; *E* isomer, 68%), −7.5 (s; *Z* isomer, 32%). FT-IR (cm^{-1}): ν 3050 (w), 2924 (w), 2859 (w), 2359 (w), 2328 (w), 1738 (w), 1591 (m), 1520 (w), 1476 (w), 1443 (w), 1370 (w), 1265 (s), 1229 (w), 1200 (w), 1107 (w), 1074 (w), 1028 (w), 997 (w), 972 (w), 895 (w), 779 (m), 762 (w), 731 (s). HR-MS (ESI-Q-TOF): calcd for $C_{22}H_{23}NP$ 332.1563; found 332.1564.

Data for **3f** are as follows. Mp: 64.3−65.6 °C. *Since not all ^{1}H and ^{13}C NMR resonances of E-**3f** and Z-**3f** can be distinguished, one set of signals is reported (integrals normalized separately for each isomer).* ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.32 (t, $^3J_{H,P}$ = 7.7 Hz, 4H; P-Ar*H* (*E*)), 7.24−7.15 (m, 8H; C-*m*-Ar*H* (*E*), Ar*H* (*Z*)), 7.12−7.02 (m, 12H; P-Ar*H* (*E*), C-*p*-Ar*H* (*E*), Ar*H* (*Z*)), 7.00 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,P}$ = 1.6 Hz, 2H; C-*o*-Ar*H* (*E*)), 3.55 (s, 3H; CN-CH_3 (*Z*)), 3.24 (d, $^4J_{H,P}$ = 1.9 Hz, 3H; CN-CH_3 (*E*)), 2.30 (s, 6H; P-C_6H_4-CH_3 (E,Z)). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 179.6 (s; *C*N-CH_3), 139.1 (s; P-Ar*C*-CH_3), 137.8 (d, $J_{C,P}$ = 25.4 Hz; *ipso*-ArC), 134.8 (d, $J_{C,P}$ = 20.0 Hz; P-ArC (*E*)), 134.0 (d, $J_{C,P}$ = 20.0 Hz; P-ArC (*Z*)), 131.0 (d, $J_{C,P}$ = 7.3 Hz; *ipso*-ArC), 130.5 (d, $J_{C,P}$ = 7.3 Hz; *ipso*-ArC), 129.6 (s; ArC), 129.5 (s; ArC), 129.2 (s; ArC), 129.1 (s; ArC), 128.2 (s; ArC), 128.1 (s; ArC), 127.9 (d, $J_{C,P}$ = 2.7 Hz; ArC), 127.7 (s; ArC), 127.5 (s; ArC), 127.1 (d, $J_{C,P}$ = 4.5 Hz; C-*o*-ArC (*E*)), 43.4 (d, $^3J_{C,P}$ = 32.7 Hz; CN-CH_3 (*Z*)), 43.2 (d, $^3J_{C,P}$ = 8.2 Hz; CN-CH_3 (*E*)), 21.5 (d, $^5J_{C,P}$ = 9.1 Hz; P-Ar*C*-CH_3 (E,Z)). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 6.3 (s; *E* isomer, 76%), −8.8 (s; *Z* isomer, 24%). FT-IR (cm^{-1}): ν 3063 (w), 3032 (w), 3015 (w), 2961 (m), 2910 (m), 2854 (w), 1653 (w), 1632 (w), 1591 (s), 1560 (w), 1524 (w), 1495 (s), 1439 (s), 1394 (m), 1306 (m), 1259 (s), 1202 (m), 1186 (m), 1099 (s), 1092 (s), 1070 (s), 1018 (s), 972 (m), 935 (m), 897 (m), 866 (w), 843 (m), 797 (s), 762 (s), 700 (s), 673 (m), 652 (s), 642 (s), 629 (s), 615 (s), 552 (w), 536 (s), 503 (s), 492 (s), 451 (s), 420 (m), 401 (s). HR-MS (ESI-Q-TOF): calcd for $C_{22}H_{23}NP$ 332.1563; found 332.1562.

Hydrolysis Study of 3a−c. **3** (0.02 g, 1.00 equiv) was dissolved in 0.6 mL of acetone in an NMR tube. Next, a solution of H_2O in acetone (10%) was added. The mixture was vigorously shaken and subsequently kept at room temperature, during which the reaction mixture was monitored using ^{31}P NMR spectroscopy. Using this methodology, systematically H_2O was added to the mixture, which was kept at room temperature during the described time span. **3a**: (1) 0.50 equiv, 21 h; (2) 0.50 equiv, 68.5 h; (3) 1.00 equiv, 29 h; (4) 2.00 equiv, 26.5 h; (5) 4.00 equiv, 18.5 h; (6) 8.03 equiv, 24.5 h. (7) 481.7 equiv, 22.5 h. Observed hydrolysis (% **3a**:% Ph_2PH, time of measurement): (1) 97:0, 21 h; (2) 95:0, 89 h; (3) 91:0, 118 h; (4) 89:0, 144 h; (5) 85:1, 163 h; (6) 85:1, 187 h; (7) 62:4, 210 h. **3b**: (1) 0.50 equiv, 18 h; 92) 0.50 equiv, 49 h; (3) 3.00 equiv, 24 h; (4) 12.1 equiv, 25 h; (5) 461.67 equiv, 16 days. Observed hydrolysis (% **3b**:% Ph_2PH, time of measurement): (1) 95:0, 18 h; 92) 91:0, 65 h; 93) 88:1, 91 h; (4) 84:2, 115 h; (5) 36:6, 524 h. **3c**: (1) 0.46 equiv, 47.5 h; 92) 2.25 equiv, 24 h; (3) 16.9 equiv, 23.5 h; (4) 563.34 equiv, 72 h). Observed hydrolysis (% **3c**:% Ph_2PH, time of measurement): (1) 95:0, 41 h; (2) 94:0, 69 h; (3) 92:1, 91 h; (4) 72:3, 165 h.

Acid Stability Study of 3a. **3a** (0.0203 g, 0.066 mmol, 1.00 equiv) was dissolved in 0.4 mL of DCM to give a yellowish solution. Addition of a solution of TfOH in DCM (0.23 mL of a 0.28 M solution, 0.064 mmol, 0.98 equiv) provided a bright yellow solution, which was vigorously shaken and kept at room temperature for 20 h, during which the reaction was monitored using ^{31}P NMR spectroscopy. Next, again TfOH in DCM (0.23 mL of a 0.28 M solution, 0.064 mmol, 0.98 equiv) was added. The mixture was vigorously shaken and kept at room temperature for 24 h, during which the reaction was monitored using ^{31}P NMR spectroscopy. Excess triethylamine (0.20 mL, 1.43 mmol, 21.74 equiv) was added to the mixture at 0 °C, resulting in a light yellow solution of pure **3a**.

Acid-Catalyzed Hydrolysis Study of 3a. **3a** (0.0267 g, 0.088 mmol, 1.00 equiv) was dissolved in 0.6 mL of DCM to give a yellowish solution. Addition of a solution of TfOH in DCM (31 μL of a 0.28 M solution, 0.009 mmol, 0.10 equiv) provided a more intensely yellow solution, which was vigorously shaken and kept at room temperature for 1 h. Subsequently, H_2O (0.8 μL, 0.044 mmol, 0.50 equiv) was added to the mixture, which then was vigorously shaken and kept at room temperature for 2 days, during which the reaction was monitored using ^{31}P NMR spectroscopy. Next, excess H_2O (5.6 μL, 0.310 mmol, 3.52 equiv) was added to the mixture. After vigorous shaking, the mixture was kept at room temperature for 24 days. Observed hydrolysis (% **3a**:% Ph_2PH, time of measurement): (1) 86:1, 17 h; (2) 76:3, 60 h; (3) 74:3, 108 h; (4) 68:5, 248 h; (5) 58:9, 603 h; (6) 49:12, 1251 h.

Oxidation Study of 3a. Under an N_2 atmosphere, **3a** (0.012 g, 0.04 mmol, 1.00 equiv) was dissolved in 0.6 mL of acetone. Stepwise, O_2 (21% in air) was bubbled manually through the mixture with a rate of approximately 6 bubbles per second using a needle with an inner diameter of 1.194 mm. During additions, the mixture was kept in a water bath at room temperature to inhibit acetone evaporation. After each addition, the NMR tube was sealed using a screw cap and the reaction mixture was monitored using ^{31}P NMR spectroscopy. Using this methodology, systematically O_2 (21% in air) was added to the mixture at room temperature over the described intervals: (1) O_2 (21% in air, 1 mL, 8.73 μmol, 0.22 equiv), 30 s; (2) O_2 (21% in air, 1 mL, 8.73 μmol, 0.22 equiv), 30 s; (3) O_2 (21% in air, 2 mL, 17.47 μmol, 0.44 equiv), 60 s; (4) O_2 (21% in air, 2 mL, 17.47 μmol, 0.44 equiv), 60 s; (5) O_2 (21% in air, 4 mL, 34.94 μmol, 0.87 equiv), 2 min; (6) O_2 (21% in air, 4 mL, 34.94 μmol, 0.87 equiv), 2 min; (7) O_2 (21% in air, 8 mL, 69.88 μmol, 1.75 equiv), 4 min; (8) O_2 (21% in air, 8 mL, 69.88 μmol, 1.75 equiv), 4 min; (9) O_2 (21% in air, 16 mL, 0.140 mmol, 3.49 equiv), 8 min; (10) O_2 (21% in air, 16 mL, 0.140 mmol, 3.49 equiv), 8 min. From addition 7 onward, a white solid started to precipitate. After the additions, the mixture was fully oxidized by dissolving the mixture in 10 mL of acetone (technical grade) and stirring the resulting solution under a closed air atmosphere for 42 h at room temperature. Subsequently, the reaction vessel was opened to the external air atmosphere and stirred for an additional 173.5 h. The resulting solution was evaporated to provide a white oil. Observed oxidation (% **3a**, time of measurement): (1) 95, 17 min; (2) 86, 24 min; (3) 82, 30 min; (4) 74, 37 min; (5) 68, 46 min.;

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(6) 61, 55 min; (7) 56, 66 min; (8) 52, 77 min; (9) 49, 91 min; (10) 44, 107 min; (11) 4, 46 h; (12) 0, 220 h.

(((*N*-Methyl)arylimidoyl)diarylphosphanyl)-(pentamethylcyclopentadienyl)rhodium(III) Dichlorides 4a,c,e. Under an argon atmosphere, a solution of **3** (102 mg 0.34 mmol, 2.4 equiv) in 9 mL of DCM was added to a red-brown solution of $[RhCp^*Cl_2]_2$ (87 mg, 0.14 mmol, 1.0 equiv) in 5 mL of DCM. The resulting red-brown solution was stirred for 30 min at room temperature. Evaporation of the obtained red solution provided a red-orange solid, which was washed with 3 × 5 mL of Et_2O to provide **4** as an orange solid (**4a**, 90%; **4c**, 68%; **4e**, 92%). For crystallization, subsequently Et_2O and pentane were diffused into a DCM solution at room temperature. Next, the solution was slowly cooled to provide red needles.

Data for **4a** are as follows. Mp: 164.6 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.71 (s, 5H; P-Ar*H*), 7.18 (s, 5H; P-Ar*H*), 6.99 (s, 3H; C-*o*,*p*-Ar*H*), 6.92 (s, 2H; C-*m*-Ar*H*), 3.36 (s, 3H; NCH_3), 1.44 (s, 15H; Cp*-CCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 137.0 (d, $^2J_{C,P}$ = 11.8 Hz, P-*o*-ArC), 135.4 (d, $^1J_{C,P}$ = 22.7 Hz; P-*ipso*-ArC), 130.2 (s; P-*p*-ArC), 127.8 (s; C-*p*-ArC), 127.7 (s; C-*o*-ArC), 127.4 (s; P-*m*-ArC), 127.0 (s; C-*m*-ArC), 99.7 (d, $^1J_{C,Rh}$ = 5.5 Hz; Cp*-CCH$_3$), 43.1 (d, $^3J_{C,P}$ = 21.8 Hz; CN-CH$_3$), 9.0 (s; Cp*-CCH_3), signals for C-*ipso*-ArC and *C*N-CH$_3$ are unresolved. ^{31}P NMR (161.98 MHz, DCM): δ 37.3 (d, $^1J_{P,Rh}$ = 146.6 Hz; **4a**, 96%), −2.2 (d, $^1J_{P,Rh}$ = 113.0 Hz; **5a**, 4%). FT-IR (cm^{-1}): ν 3055 (w), 2961 (w), 2914 (w), 1609 (m), 1609 (m), 1572 (w), 1489 (m), 1479 (m), 1433 (s), 1383 (m), 1369 (w), 1261 (m), 1209 (m), 1200 (m), 1188 (m), 1157 (m), 1092 (s), 1072 (s), 1022 (s), 970 (m), 951 (m), 860 (w), 800 (s), 764 (s), 743 (s), 690 (s), 648 (m), 611 (m), 550 (s), 511 (s), 494 (s), 469 (s), 451 (s), 430 (m), 401 (s). HR-MS (ESI-Q-TOF): calcd for $C_{30}H_{34}Cl_2NPRh^+$ 612.0855; found 612.0873.

Data for **4c** are as follows. Mp: 200.7 °C dec. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.71 (br. s, 4H; P-Ar*H*), 7.42−7.09 (br. m, 8H; C-*o*-Ar*H*, P-Ar*H*), 7.02 (d, $^3J_{H,H}$ = 7.1 Hz, 2H; C-*m*-Ar*H*), 3.32 (d, $^3J_{H,P}$ = 2.8 Hz, 3H; CN-CH_3), 1.43 (d, $^3J_{H,Rh}$ = 3.5 Hz, 15H; Cp*-CCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 175.1 (d, $^1J_{C,P}$ = 57.2 Hz; *C*N-CH$_3$), 139.1 (d, $^1J_{C,P}$ = 20.9 Hz; P-*ipso*-ArC), 135.4 (br. s; P-ArC), 130.6 (s; P-ArC), 129.8 (q, $^2J_{C,F}$ = 32.7 Hz; C-*p*-ArC), 127.7 (s; C-*m*-ArC), 124.6 (q, $^4J_{C,F}$ = 3.6 Hz; C-*o*-ArC), 124.2 (q, $^1J_{C,F}$ = 272.5 Hz; *C*F$_3$), 99.8 (dd, $^1J_{C,Rh}$ = 6.4 Hz, $^2J_{C,P}$ = 2.7 Hz; Cp*-CCH$_3$), 43.2 (d, $^3J_{C,P}$ = 20.9 Hz; CN-CH$_3$), 9.0 (s; Cp*-CCH_3), signals for C-*ipso*-ArC and one P-Ar*C* are unresolved. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −63.3 (s). ^{31}P NMR (161.98 MHz, DCM): δ 35.1 (d, $^1J_{P,Rh}$ = 146.9 Hz). FT-IR (cm^{-1}): ν 3057 (w), 2989 (w), 2953 (w), 2908 (w), 1624 (w), 1614 (w), 1572 (w), 1508 (m), 1479 (m), 1448 (m), 1433 (s), 1406 (m), 1369 (m), 1321 (s), 1263 (w), 1205 (w), 1188 (m), 1165 (s), 1122 (s), 1109 (s), 1090 (m), 1067 (s), 1020 (s), 997 (m), 972 (m), 933 (w), 924 (w), 837 (s), 800 (w), 743 (s), 696 (s), 689 (s), 663 (m), 619 (m), 606 (m), 550 (s), 509 (s), 498 (s), 465 (s), 449 (s), 432 (m). HR-MS (ESI-Q-TOF): calcd for $C_{31}H_{33}Cl_2F_3NPRh^+$ 680.0705; found 680.0705.

Data for **4e** are as follows. Mp: 139.6 °C dec. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.66−7.35 (m, 5H; P-Ar*H*), 7.22−6.95 (m, 6H; C-Ar*H*, P-Ar*H*), 6.91 (s, 2H; C-Ar*H*), 3.35 (s, 3H; CN-CH_3), 2.19 (br. s, 6H; P-ArCH_3), 1.43 (d, $^3J_{H,Rh}$ = 2.8 Hz, 15H; Cp*-CCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 176.6 (d, $^3J_{C,P}$ = 60.9 Hz; *C*N-CH$_3$), 135.6 (d, $^1J_{C,P}$ = 20.9 Hz; P-*ipso*-ArC), 134.4 (d, $J_{C,P}$ = 2.7 Hz; P-ArC), 130.9 (s; P-ArC), 129.9 (d, $J_{C,P}$ = 12.7 Hz; P-ArC), 129.1 (d, $J_{C,P}$ = 11.8 Hz; P-ArC), 127.7 (s; C-ArC), 127.5 (s; C-ArC), 126.9 (s; C-ArC), 99.6 (dd, $^1J_{C,Rh}$ = 6.4 Hz, $^2J_{C,P}$ = 2.7 Hz; Cp*-CCH$_3$), 43.1 (d, $^3J_{C,P}$ = 21.8 Hz; CN-CH$_3$), 21.5 (s; P-ArCH$_3$), 9.0 (d, $^2J_{C,Rh}$ = 1.8 Hz; Cp*-CCH$_3$), signals for C-*ipso*-ArC and P-Ar *C*-CH$_3$ are unresolved. ^{31}P NMR (161.98 MHz, DCM): δ 34.7 (d, $^1J_{P,Rh}$ = 144.6 Hz; **4e**, 94%), −12.1 (d, $^1J_{P,Rh}$ = 114.7 Hz; **5e**, 6%). FT-IR: ν = 2962 (m), 2907 (w), 1479 (w), 1443 (w), 1400 (w), 1258 (s), 1078 (s), 1011 (s), 864 (m), 789 (s), 690 (s), 662 (m), 611 (w), 557 (m), 542 (m), 480 (m), 465 (s), 465 (s). HR-MS (ESI-Q-TOF): calcd for $C_{32}H_{38}Cl_2NPRh^+$ 640.1168; found 640.1163.

Chloro(((*N*-methyl)arylimidoyl)diarylphosphanyl)-(pentamethylcyclopentadienyl)rhodium(III) Trifluoromethylsulfonates 6a,c,e. Under an argon atmosphere, to a solution of **3** (0.31 mmol, 2.1 equiv) in 14 mL of DCM was added $[RhCp^*Cl_2]_2$ (95 mg, 0.15 mmol, 1.0 equiv) to provide a red solution, which was stirred for 30 min at room temperature. Next, AgOTf (79 mg, 0.30 mmol, 2.0 equiv) was added and the resulting suspension was stirred for 60 min at room temperature in the absence of light, during which the mixture turned bright orange. Filtration provided an orange-red solution, which was evaporated to provide a yellow-orange solid. After washing (**6a**,**e**: 3 × 5 mL of Et_2O; **6c**, 3 × 5 mL of pentane), **6** was obtained as an orange powder (**6a**. quantitative; **6c**, 97%; **6e**, 97%).

Data for **6a** are as follows. Mp: 138.8 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.66−7.59 (m, 8H; P-Ar*H*), 7.47−7.42 (m, 3H; C-*o*-Ar*H*, P-Ar*H*), 7.36 (t, $^3J_{H,H}$ = 6.9 Hz, 2H; C-*m*-Ar*H*), 7.23 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; C-*o*-Ar*H*), 3.69 (d, $^3J_{H,Rh}$ = 3.8 Hz; N−CH_3), 1.70 (d, $^3J_{H,Rh}$ = 3.8 Hz; Cp*-CCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 190.9 (dd, $^1J_{C,P}$ = 50.0 Hz, $^2J_{C,Rh}$ = 2.7 Hz; *C*N-CH$_3$), 136.7 (d, $^2J_{C,P}$ = 11.8 Hz; P-*m*-ArC), 133.8 (d, $^4J_{C,P}$ = 2.7 Hz; P-*p*-ArC), 133.0 (d, $^3J_{C,P}$ = 10.9 Hz; P-*o*-ArC), 132.9 (d, $^4J_{C,P}$ = 2.7 Hz; P-*p*-ArC), 132.3 (dd, $^3J_{C,Rh}$ = 7.3 Hz, $^2J_{C,P}$ = 1.8 Hz; C-*ipso*-ArC), 131.8 (s; C-*p*-ArC), 130.4 (d, $^3J_{C,P}$ = 10.9 Hz; P-*m*-ArC), 129.4 (d, $^2J_{C,P}$ = 11.8 Hz; P-*o*-ArC), 129.2 (s; C-*m*-ArC), 127.5 (d, $^2J_{C,P}$ = 1.8 Hz; C-*o*-ArC), 123.7 (d, $^1J_{C,P}$ = 45.4 Hz; P-*ipso*-ArC), 121.2 (q, $^1J_{C,F}$ = 320.6 Hz; O$_3$SCF_3), 120.7 (d, $^1J_{C,P}$ = 36.3 Hz; P-*ipso*-ArC), 99.8 (dd, $^1J_{C,Rh}$ = 7.3 Hz, $^2J_{C,P}$ = 2.7 Hz; Cp*-*C*CH$_3$), 44.7 (d, $^2J_{C,Rh}$ = 18.2 Hz; NCH$_3$), 9.6 (d, $^2J_{C,Rh}$ = 1.8 Hz; Cp*-CCH$_3$). ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −78.2 (s). ^{31}P NMR (161.98 MHz, DCM): δ −9.1 (d, $^1J_{P,Rh}$ = 113.4 Hz). FT-IR (cm^{-1}): ν 3065 (w), 2978 (w), 2908 (w), 1603 (w), 1479 (w), 1439 (m), 1381 (w), 1265 (s), 1240 (s), 1221 (s), 1188 (w), 1140 (s), 1097 (m), 1078 (m), 1030 (s), 997 (m), 951 (w), 854 (w), 847 (m), 814 (w), 752 (s), 719 (m), 692 (s), 635 (s), 565 (m), 517 (s), 482 (s), 463 (s), 440 (s). HR-MS (ESI-Q-TOF): calcd for $C_{30}H_{33}ClNPRh^+$ 576.1089; found 576.1112.

Data for **6c** are as follows. Mp: 120.9−128.5 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.74−7.66 (m, 6H; P-*o*,*p*-Ar*H*), 7.66−7.58 (m, 4H; P-*m*-Ar*H*, C-*o*-Ar*H*), 7.53−7.46 (m, 2H; P-*m*-Ar*H*), 7.41 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; C-*m*-Ar*H*), 3.68 (d, $^3J_{H,Rh}$ = 4.1 Hz, 3H; CN-CH_3), 1.71 (d, $^3J_{H,Rh}$ = 4.7 Hz, 15H; Cp*-CCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 189.6 (dd, $^1J_{C,P}$ = 50.0 Hz, $^2J_{C,Rh}$ = 4.5 Hz; *C*N-CH$_3$), 136.8 (d, $^2J_{C,P}$ = 11.8 Hz; P-*m*-ArC), 135.1 (d, $^3J_{C,Rh}$ = 7.3 Hz; C-*ipso*-ArC), 134.0 (d, $^4J_{C,P}$ = 2.7 Hz; P-*p*-ArC), 133.1 (t, $^2J_{C,F}$ = 33.6 Hz; C-*p*-ArC), 133.1 (d, $^2J_{C,P}$ = 10.9 Hz; P-*o*-ArC), 130.6 (d, $^2J_{C,P}$ = 10.9 Hz; P-*o*-ArC), 129.5 (d, $^3J_{C,P}$ = 10.9 Hz; P-*m*-ArC), 128.4 (s; C-*m*-ArC), 126.2 (q, $^3J_{C,F}$ = 3.6 Hz; C-*o*-ArC), 123.4 (q, $^1J_{C,F}$ = 272.6 Hz; C-Ar-*C*F$_3$), 123.1 (d, $^1J_{C,P}$ = 44.5 Hz; P-*ipso*-ArC), 121.2 (q, $^1J_{C,F}$ = 320.6 Hz; O$_3$SCF_3), 120.5 (d, $^1J_{C,P}$ = 34.5 Hz; P-*ipso*-ArC), 99.9 (dd, $^1J_{C,Rh}$ = 7.3 Hz, $^2J_{C,P}$ = 2.7 Hz; Cp*-CCH$_3$), 45.1 (d, $^2J_{C,Rh}$ = 18.2 Hz; CN-CH$_3$), 9.6 (s; Cp*-CCH$_3$), signal for one P-*p*-ArC is unresolved. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −63.2 (s; C*F*$_3$), −78.2 (s; O$_3$SC*F*$_3$). ^{31}P NMR (161.98 MHz, DCM): δ −5.0 (d, $^1J_{P,Rh}$ = 114.7 Hz). FT-IR (cm^{-1}): ν 3072 (w), 2926 (w), 1616 (w), 1481 (w), 1456 (w), 1437 (w), 1406 (w), 1379 (w), 1323 (s), 1258 (s), 1223 (m), 1128 (m), 1113 (m), 1101 (m), 1067 (m), 1067 (m), 1030 (s), 993 (m), 993 (m), 839 (m), 839 (m), 746 (m), 746 (m), 719 (w), 690 (m), 636 (s), 571 (m), 527 (m), 517 (m), 492 (m), 474 (m), 444 (m). HR-MS (ESI-Q-TOF): calcd for $C_{31}H_{32}ClF_3NPRh^+$ 644.0963; found 644.0967.

Data for **6e** are as follows. Mp: 153.2 °C dec. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.59−7.53 (m, 1H; P-Ar*H*), 7.48−7.30 (m, 10H; P-Ar*H*, C-*m*,*p*-Ar*H*), 7.23 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; C-*o*-Ar*H*), 3.7 (d, $^3J_{H,Rh}$ = 4.1 Hz, 3H; CN-CH_3), 2.45 (s, 3H; P-Ar-CH_3), 2.29 (s, 3H; P-Ar-CH_3), 1.70 (d, $^3J_{H,Rh}$ = 4.4 Hz, 15H; Cp*-CCH_3). ^{13}C{^{1}H} NMR (125.78 MHz, $CDCl_3$): δ 191.0 (dd, $^1J_{C,P}$ = 50.0 Hz, $^2J_{C,Rh}$ = 3.6 Hz; *C*N-CH$_3$), 140.7 (d, $^3J_{C,P}$ = 10.9 Hz; P-ArC-CH$_3$), 139.2 (d, $^3J_{C,P}$ = 10.9 Hz; P-Ar *C*-CH$_3$), 137.0 (d, $J_{C,P}$ = 10.9 Hz; P-ArC), 134.5 (d, $J_{C,P}$ = 2.7 Hz; P-ArC), 133.8 (s; P-ArC), 132.9 (d, $J_{C,P}$ = 10.9 Hz; P-ArC), 132.4 (d, $^3J_{C,Rh}$ = 7.3 Hz; C-*ipso*-ArC), 131.7 (s; C-*p*-ArC), 130.3 (dd, $^2J_{C,P}$ = 11.4 Hz, $^3J_{C,Rh}$ = 3.2 Hz; P-*o*-ArC), 129.1 (s; C-*m*-ArC), 127.6 (s; C-*o*-ArC), 123.6 (d, $^1J_{C,P}$ = 43.6 Hz; P-*ipso*-ArC), 121.2 (q, $^1J_{C,F}$ = 320.6 Hz; O$_3$SCF_3), 120.4 (d, $^1J_{C,P}$ = 36.3 Hz; P-*ipso*-ArC), 99.7 (dd, $^1J_{C,Rh}$ = 7.3 Hz, $^2J_{C,P}$ = 2.7 Hz; Cp*-CCH$_3$), 44.6 (d, $^2J_{C,Rh}$ = 19.1 Hz;

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CN-CH_3), 21.5 (d, $^4J_{C,P}$ = 1.8 Hz; P-Ar-CH_3), 9.6 (s; Cp*-CCH_3), signals for three P-*p*-ArC are unresolved. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −78.6 (s). ^{31}P NMR (161.98 MHz, DCM): δ −8.5 (d, $^1J_{P,Rh}$ = 112.4 Hz). FT-IR (cm^{-1}): ν 3065 (w), 2962 (w), 2920 (w), 1655 (w), 1593 (w), 1541 (w), 1474 (m), 1447 (m), 1375 (m), 1319 (w), 1259 (s), 1223 (s), 1205 (s), 1146 (s), 1107 (s), 1080 (s), 1030 (s), 995 (s), 864 (w), 789 (s), 762 (s), 690 (s), 636 (s), 569 (s), 548 (s), 517 (s), 496 (w), 474 (m), 446 (s). HR-MS (ESI-Q-TOF): calcd for $C_{32}H_{37}ClNPRh^+$ 604.1402; found 604.1409.

[(((*N*-Methyl)phenylimidoyl)diphenylphosphanyl)-(pentamethylcyclopentadienyl)rhodium(III)(trifluoromethylsulfonate)][poly(disilver(I)tris-(trifluoromethanesulfonate)(methylene chloride))] (7a). Under an argon atmosphere, to a solution of **3a** (92 mg 0.30 mmol, 2.0 equiv) in 15 mL of DCM was added $[RhCp^*Cl_2]_2$ (94 mg 0.15 mmol, 1.0 equiv) to provide a red solution, which was stirred for 30 min at room temperature. Next, AgOTf (317 mg, 1.23 mmol, 8.2 equiv) was added and the resulting suspension was stirred for 60 min at room temperature in the absence of light, during which the mixture turned yellow. Filtration provided an orange-red solution, which was evaporated to provide an orange-red solid. After washing with 20 mL of pentane, **7a** was obtained as a yellow solid (306 mg, 0.21 mmol, 71%). For crystallization, slow diffusion of pentane (55 mL/mmol of compound) into a DCM solution (45 mL/mmol of compound) at room temperature provided red blocks. Mp: 178.6 °C. ^{1}H NMR (500.23 MHz, $CDCl_3$): δ 7.76−7.63 (m, 6H; P-*o*,*p*-Ar*H*), 7.49−7.46 (m, 5H; P-*m*-Ar*H*, C-*p*-Ar*H*), 7.40 (t, $^3J_{H,H}$ = 7.7 Hz, 2H; C-*m*-Ar*H*), 7.33 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; C-*o*-Ar*H*), 4.01 (d, $^3J_{H,Rh}$ = 4.4 Hz, 3H; CN-CH_3), 1.72 (d, $^3J_{H,Rh}$ = 5.0 Hz, 15H; Cp*-CCH_3). $^{13}C\{^1H\}$ NMR (125.78 MHz, $CDCl_3$): δ 193.9 (dd, $^1J_{C,P}$ = 48.1 Hz, $^2J_{C,Rh}$ = 3.6 Hz; *C*N-CH_3), 136.2 (dd, $^3J_{C,P}$ = 11.8 Hz, $^4J_{C,Rh}$ = 3.6 Hz; P-*m*-ArC), 134.4 (d, $^4J_{C,P}$ = 8.2 Hz; P-*p*-ArC), 133.6 (d, $^4J_{C,P}$ = 7.3 Hz; P-*p*-ArC), 133.3 (d, $^2J_{C,P}$ = 10.9 Hz; P-*o*-ArC), 132.3 (s; C-*p*-ArC), 132.1 (d, $^2J_{C,P}$ = 6.4 Hz; C-*ipso*-ArC), 130.8 (d, $^2J_{C,P}$ = 8.2 Hz; P-*o*-ArC), 129.7 (d, $^3J_{C,P}$ = 10.7 Hz; P-*m*-ArC), 129.3 (s; C-*m*-ArC), 127.7 (d, $^3J_{C,P}$ = 1.8 Hz; C-*o*-ArC), 100.8 (dd, $^1J_{C,Rh}$ = 8.2 Hz, $^2J_{C,P}$ = 2.7 Hz; Cp*-CCH_3), 46.1 (d, $^2J_{C,Rh}$ = 17.3 Hz; CN-CH_3), 9.8 (s; Cp*-CCH_3), signals for P-*ipso*-ArC are unresolved. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ −78.2 (d, $^4J_{F,Rh}$ = 12.1 Hz; Rh-OS(O_2)CF_3). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ −9.9 (d, $^1J_{P,Rh}$ = 111.2 Hz). FT-IR (cm^{-1}): ν 3065 (w), 2995 (w), 1580 (w), 1483 (w), 1437 (m), 1379 (w), 1304 (s), 1261 (s), 1229 (s), 1202 (s), 1159 (s), 1144 (s), 1099 (m), 1082 (m), 1030 (s), 1005 (s), 951 (m), 926 (w), 771 (m), 754 (m), 733 (m), 689 (s), 635 (s), 573 (m), 557 (m), 536 (w), 515 (s), 476 (s), 463 (m), 442 (m). HR-MS (ESI-Q-TOF): calcd for $C_{31}H_{33}F_3NO_3PRhS^+$ 690.0920; found 690.0915.

[(1,3-P,N)Ru^{II}]-Catalyzed Hydrations of Benzonitrile. *Protocol 1.* $[Ru(Ar)Cl_2]_2$ (Ar = *p*-cym, C_6Me_6, C_6H_5Me, Cp*; 0.025 mmol, 5 mol %) and ligand **3a** or Ph_2PPy (0.05 mmol, 5 mol %) were dissolved in DME (0.5 mL) under an argon atmosphere and stirred for 30 min. Benzonitrile (105 μL, 1.02 mmol, 1.0 equiv) and H_2O (36 μL, 1.99 mmol, 2.0 equiv) were added and the sealed vessel was stirred at 180 °C for 3 h.

Protocol 2. $[Ru(p\text{-cym})Cl_2]_2$ (16 mg, 0.026 mmol, 5 mol % [Ru]) and ligand **3a** or Ph_2PPy (0.052 mmol, 5 mol %) were dissolved in benzonitrile (105 μL, 1.02 mmol, 1.0 equiv) under an argon atmosphere and stirred for 30 min. H_2O (3.0 mL, 166 mmol, 163 equiv) was added and the sealed vessel was stirred at 100 °C for 24 h.

Protocol 3. $[Ru(p\text{-cym})Cl_2]_2$ (15 mg, 0.024 mmol, 1.4 mol % of Ru) and ligand (0.050 mmol, 1.4 mol %) were dissolved in benzonitrile (370 μL, 3.58 mmol, 1.0 equiv) under an argon atmosphere and stirred for 30 min. H_2O (130 μL, 7.2 mmol, 2.0 equiv) was added and the sealed vessel was stirred at 180 °C for 3 h.

Analysis. After they were cooled to room temperature, the mixtures were extracted with *i*-PrOH under atmospheric conditions and analyzed by GC (internal standard naphthalene).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00057.

Additional synthetic details, NMR spectra, and geometries of computed structures (PDF)

X-ray crystallographic data for **4a** (CCDC-1487761), **4e** (CCDC-1487762), **6a** (CCDC-1487763), and **7a** (CCDC-1487764) (CIF)

Cartesian coordinates for calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

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