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Synthesis, Coordination Chemistry, and Cooperative Activation of H_2 with Ruthenium Complexes of Proton-Responsive METAMORPhos Ligands

CLUSTER ISSUE

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The synthetic scope of proton-responsive sulfonamidophosphorus (METAMORPhos) ligands is expanded and design principles for the selective formation of particular tautomers, ion pairs, or double condensation products are elucidated. These systems have been introduced in the coordination sphere of Ru for the first time, thereby enabling the exclusive coordination as a monoanionic P,O chelate. Depending on the Ru precursor, halide-bridged dinuclear species **3**–**5** or cymene-derived piano-stool complexes **6**–**9** are isolated. The METAMORPhos framework is shown to play a role in the heterolytic cleavage of H_2, with species **7** converted into neutral monohydride **10**. Substitution chemistry with cymene complex **7** has also been examined, thereby giving rise to tetrakis(acetonitrile) adduct **11**. Introduction of a second equivalent of METAMORPhos ligand to this species yielded the bis(ligated) derivative **13**, for which variable-temperature (VT) NMR spectroscopy indicates coalescence of the phosphine donors at high temperature. Solid-state structures of **3**, **6**, **11**, and **13** are presented to establish the precise bonding situation of the inorganic PNSO framework within METAMORPhos upon coordination as a proton-responsive monoanionic P,O chelate.

Introduction

Since Noyori et al. unveiled an outer-sphere mechanism to be operative for transfer hydrogenation with particular aminoamide chelate ligands,[1] proton-responsive ligands have attracted much attention as reactive scaffolds for selective bond-activation processes and cooperative catalysis.[2] The proton-responsive character is brought about by acido–basic moieties that can be reversibly deprotonated during catalytic turnover, thereby allowing bioinspired bifunctional substrate activation and conversion.[3]

More recently, dehydrogenations and dehydrogenative coupling reactions based on the same proton-responsive nature of suitable bifunctional metal–ligand combinations have been developed. In those reactions, the basic ligand abstracts a proton, and the metal center abstracts a hydride from the substrate. The catalytic cycle is then closed by release of hydrogen and regeneration of the initial complex. Such catalysts have been used for various atom-efficient conversions.[4] Proton-responsive ligands can also be used for "hydrogen-borrowing" reactions wherein the substrate is dehydrogenated by the catalyst, undergoes a coupling reaction, and is then hydrogenated.[5]

The proton-responsive feature might involve temporary dearomatization of functionalized pyridines,[6] the interconversion between amino/amido units within the ligand framework,[7] or pH-responsive pyridonate fragments.[8] In addition, some other concepts have been explored as well.[9] Most of these ligands currently lack a high degree of modularity to effectively tune the proton response for specific (catalytic) purposes. Hence, the applicability of these systems to address different types of conversions or substrate classes is limited. Moreover, the possibilities to introduce elements of chirality for asymmetric transformations are often hampered by cumbersome synthetic procedures.

Sulfonamidophosphorus "METAMORPhos" ligands were recently introduced as a family of highly versatile and modular building blocks for late-transition-metal complexes.[10] Their ability to act as (chiral) proton-responsive ligands in Rh-catalyzed (asymmetric) hydrogenation of functionalized alkenes was demonstrated (Scheme 1).[10a–10c] A novel cooperative mechanism for the activation of molecular dihydrogen was proposed (Scheme 2, a).[10a] The unique self-sorting behavior among complexes bearing chiral derivatives has recently been communicated.[11] Furthermore, Ir–METAMORPhos complexes were used for the base-free dehydrogenation of formic acid (Scheme 2, b). Besides the proton-responsive character of this ligand, which allowed it to act as internal

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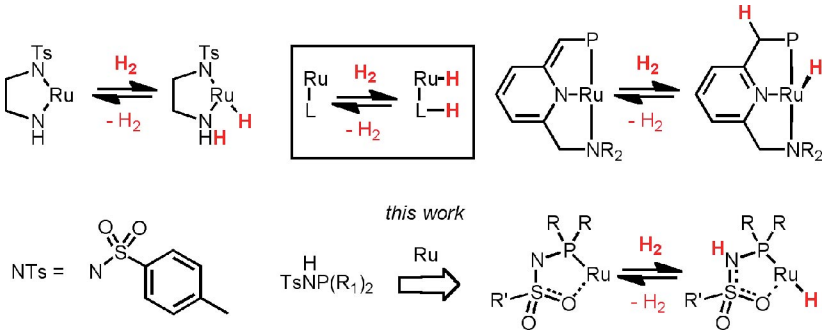
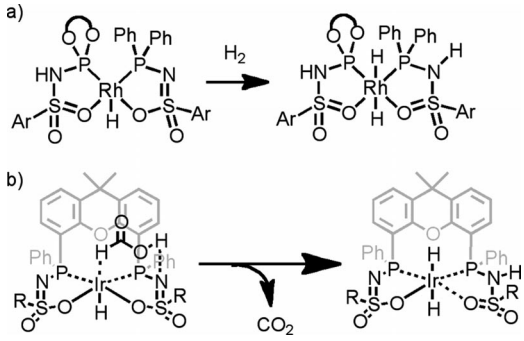


Scheme 1. Top: Proton-responsive behavior of known Ru systems[1,6] toward H_2. Bottom: Envisioned reactivity of METAMORPhos ligands.

base, its ability to function as hydrogen-bond acceptor was found to be crucial for catalyst activity.[10d] Also noteworthy is the complete inorganic PNSO backbone of these ligands in these constellations.



Scheme 2. (a) METAMORPhos as proton-responsive ligand for hydrogen splitting and (b) formic acid dehydrogenation.

Encouraged by these results, we decided to thoroughly investigate and optimize the synthetic procedures for a range of METAMORPhos ligands to establish a broader acido-basic scope and to study the coordination behavior of selected systems with ruthenium, which is often the metal of choice for catalytic transformations that involve proton-responsive ligands.[12]

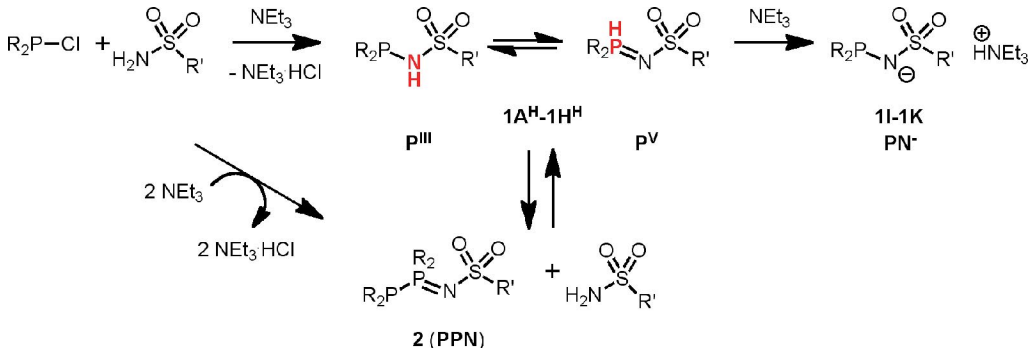
Results and Discussion

Ligand Synthesis

METAMORPhos ligands **1A**–**K** have been obtained by condensation of readily available chlorophosphorus compounds (chlorophosphines or chlorophosphites) with sulfonamides (Scheme 3). As the latter are essential building blocks for biologically active molecules, a plethora of primary sulfonamides is commercially available, which in principle could enable the (high-throughput) synthesis of many ligands, thereby allowing fine-tuning of their proton-responsive identity. So far, only a limited number from this ligand class have been reported.[10,13] Depending on the substituents on phosphorus and sulfur, different condensation products are typically obtained (Scheme 3).

Indeed, when sulfonamides are coupled to chlorophosphites, the deprotonated ligand **1**$^-$ (**PN**$^-$) is formed (as the triethylammonium salt) as the sole product, regardless of the electronic properties of the sulfonamide (Table 1, entries I–K). This tendency of phosphoramidite-based METAMORPhos systems to form strong ion pairs, which is related to the enhanced acidity of the –NH group due to the electron-withdrawing binaphthol (BINOL) auxiliary, and the resulting dinucleating nature of the **PN**$^-$ scaffolds was previously exploited in our group.[11] In contrast, employing chlorophosphines typically results in neutral METAMORPhos ligands with reduced overall acidity at nitrogen (Table 1, entries A–H). These phosphines show tautomerism due to prototropic behavior: the proton either resides on the nitrogen (**P^{III}**) or on phosphorus (**P^{V}**). Electron-donating isopropyl or *tert*-butyl groups at phosphorus (Table 1, entries F–H), stabilize the high-oxidation-state **P^{V}** tautomer, which is the only detected tautomer in solution. For chlorodiarylphosphines (Table 1, entries A–E), both tautomers can be observed by ^{31}P NMR spectroscopy, with the **P^{III}/P^{V}** ratio strongly depending on the nature of the sulfonamide R group. Electron-donating fragments favor the regular **P^{III}** tautomer, while the electron-withdrawing bis(trifluoromethyl)phenyl group leads to enhanced acidity at nitrogen, resulting in almost complete tautomer reversal to **P^{V}** as the major component in solution.

When the sulfur atom carries an electron-withdrawing organic substituent such as bis(trifluoromethyl)phenyl, the double condensation product **2** is also obtained as a by-product or even the main product.[13,14] Bulky phosphorus substituents prevent (Table 1, entries F and G) or suppress (Table 1, entry H) the occurrence of **2**. In most cases, removal of this diphosphorus compound was facile, but treatment of $ClPPh_2$ with bis(trifluoromethyl)phenyl sulfonamide provided a mixture of **1D** and **2D** from which only **2D** was obtained after purification, thus indicating a low energy barrier for self-condensation and potentially higher stability of **2D** (Table 1, entry D). Fortunately, replacement of the phenyl substituent by more bulky *o*-tolyl groups on



Scheme 3. Condensation of chlorophosphorus compounds with sulfonamides to give species **1^{H}** (as the **P^{III}** and/or **P^{V}** tautomer) or the deprotonated **1^{-}** (**PN^{-}**) derivative thereof and/or **2** (**PPN**) depending on reaction conditions and the specific substitution patterns at phosphorus and sulfur.

Table 1. Condensation between chlorophosphorus species and sulfonamides.

	R	R′	Product(s) (crude)[a]	(isolated) major (*minor*)
A	phenyl	*p*-butylphenyl	**1**	**P^{III}** (***P^{V}***)
B	phenyl	*p*-tolyl	**1**	**P^{III}** (***P^{V}***)
C	phenyl	*p*-methoxyphenyl	**1** and **2**	**P^{III}** (***P^{V}***)
D	phenyl	*m*-bis(trifluoromethyl)phenyl	**1** and **2**	**2**
E	*o*-tolyl	*m*-bis(trifluoromethyl)phenyl	**1** and **2**	**P^{V}** (***P^{III}***)
F	isopropyl	*p*-butylphenyl	**1** and **2**[b]	**P^{V}**
G	isopropyl	trifluoromethyl	**1** and **2**	**P^{V}**
H	*tert*-butyl	trifluoromethyl	**1**	**P^{V}**
I	BINOL	methyl	**1**	**PN^{-}**
J	BINOL	*p*-butylphenyl	**1**	**PN^{-}**
K	BINOL	trifluoromethyl	**1**	**PN^{-}**

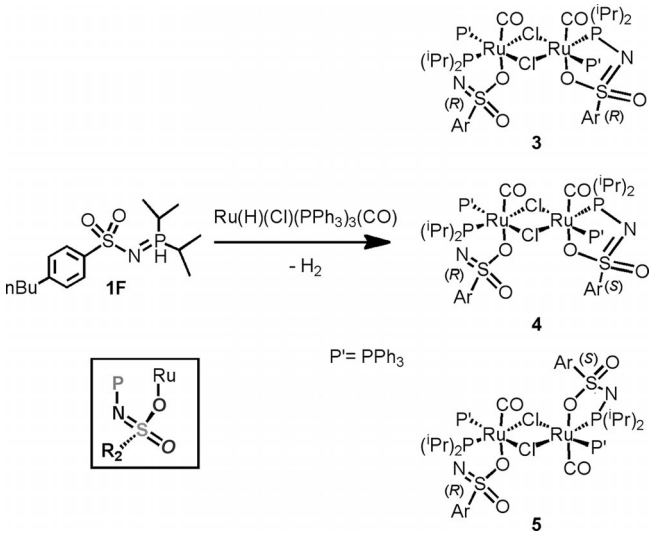
[a] After 16 h reaction. [b] Trace amount.

phosphorus and higher temperature for the coupling reaction favored the formation of neutral monophosphine **1^{H}**. Compound **1E^{H}** could be isolated in reasonable yield without any contamination of **2E**.

Coordination to a Ru^{II} Precursor Bearing an Internal Base

To date, the coordination chemistry of METAMORPhos ligands has only been detailed for group 9 metals with multiple geometries already established. The ligand can act as a neutral monodentate P donor or as monoanionic bridging P,N ligand.[10] However, no mononuclear, monoligated species bearing METAMORPhos as bidentate monoanionic P,O chelate has been established to date. Deprotonation of the –NH unit can be enforced by the addition of an external base during complexation or through the use of a metal precursor bearing an internal base such as the acetylacetonate (acac) ligand in [Ir(acac)(cod)] (cod = cyclooctadiene).[10d] We sought to expand this "intramolecular" deprotonation strategy and to enforce irreversible deprotonation, as acetylacetone was found to induce isomerization of dimeric structures due to reversible proton-transfer phenomena under certain reaction conditions.[10d] Removal of the "conjugate acid" from the reaction mixture should eliminate this process. We thus opted to investigate a metal–hydride precursor that would result in highly volatile H_2 as "conjugate acid". This concept also underlies recent applications for dehydrogenative coupling reactions.

Gratifyingly, when ligand **1F^{H}** was treated with [Ru(H)(Cl)(PPh$_3$)$_3$(CO)] in toluene under reflux conditions (Scheme 4), two sets of two doublets were observed in a 1:1.7 ratio in the ^{31}P NMR spectrum, each corresponding to one METAMORPhos [δ = 100.0 ($J_{P,P}$ = 25.5 Hz) and 97.7 ppm ($J_{P,P}$ = 24 Hz)] and one PPh$_3$ ligand [δ = 39.1 ($J_{P,P}$ = 24.0 Hz)] and 37.4 ppm ($J_{P,P}$ = 25.5 Hz)]. No hydride or –N*H* signal was apparent in the ^{1}H NMR spectrum, thus indicating the release of H_2. The two species are proposed to be isomers given the strong resemblance in their spectral features. Single crystals suitable for X-ray diffraction could be obtained by slow diffusion of diethyl ether into a dichloromethane solution. Surprisingly, the molecular structure (see Figure 1) was found to be that of chloride-bridged dimer **3**, which features the METAMORPhos ligand as anionic P,O chelate. Coordination of the oxygen atom leads to desymmetrization of the sulfonamide fragment and induces



Scheme 4. Coordination of **1F^{H}** to [Ru(H)(Cl)(PPh$_3$)$_3$(CO)] to generate **3** (and/or isomeric **4/5**) concomitant with hydrogen release. The chirality at sulfur, induced by ligand coordination to Ru, is highlighted.

chirality at the sulfur atom.[15] The dimer has exact crystallographic C_2 symmetry with both sulfur atoms of equal chirality, but the unit cell possesses an inversion center as the complex crystallizes as a true racemate. The P1–Ru–P2 angle of 100.154(15)° as well as the O1–Ru–C17 angle of 174.02(5)° exemplify the distorted-octahedral geometry around Ru. The P1–Ru–O1 angle is small at 82.39(3)°. The N–S bond length of 1.5435(14) Å indicates double-bond character.[16] The S–O1 [1.4911(11) Å; formal S–O] and S–O2 [1.4416(12) Å; S=O] bond lengths differ significantly as a consequence of the coordination of O1 to the metal. The spectroscopically observed second species is suggested to correspond to a Ru dimer with ligands of opposite chirality at the sulfur atom, either with a pseudo-C_2 axis (structure **4**) or a center of inversion (structure **5**).

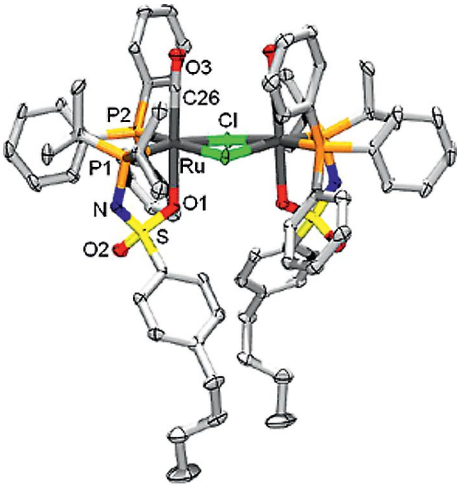
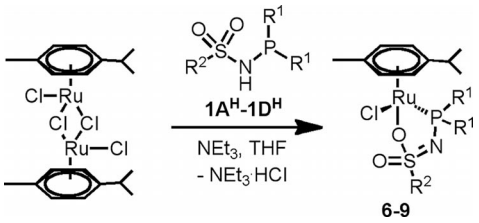


Figure 1. Solid-state structure of **3**. Hydrogen atoms have been omitted for clarity. Only the major conformation of the disordered *n*-butyl chain is shown. Selected bond lengths [Å] and angles [°]: Ru–P1 2.3096(4), Ru–P2 2.3466(4), Ru–O1 2.1485(11), Ru–C17 1.8293(16), Ru–Cl 2.4673(4), P1–N 1.6597(14), N–S 1.5435(14), S–O1 1.4911(13), S–O2 1.4416(14); P1–Ru–P2 100.15(2), P1–Ru–Cl 168.320(14), P2–Ru–Cl 86.773(14), O1–Ru–C17 174.02(5), P1–Ru–O1 82.39(3), P2–Ru–O1 93.54(3), N–S–O1 112.92(7), N–S–O2 113.44(8), Ru–C17–O3 176.64(14), P–N–S 119.30(9). Symmetry operation *i*: –*x*, *y*, 0.5 – *z*.

Formation of Ru Complexes with Piano-Stool Geometry

Because a reproducible high-yielding synthesis of **3** turned out to be cumbersome due to purification problems, we resorted to [{RuCl(cymene)(μ-Cl)}$_2$] as an alternative Ru precursor. Coordination of **1A^H** with this cymene dimer in THF in the presence of triethylamine led to quantitative formation of a single product, according to ^{31}P NMR spectroscopy, with concomitant precipitation of triethylammonium chloride. The cymene fragment is preserved within the coordination sphere of ruthenium, as deduced from the ^{1}H NMR spectrum, which suggests a piano-stool geometry for complex **6** (Scheme 5).



Scheme 5. Synthesis of piano-stool complexes **6**–**9**.

This geometry was unambiguously corroborated by X-ray crystal-structure determination; the molecular structure is depicted in Figure 2. Like for **3**, the METAMORPhos ligand is deprotonated and acts as a P,O chelate. The P–R–O1 angle of 80.20(4)° is even smaller than in dimer **3**, whereas the Ru–P bond is marginally longer at 2.3240(5) Å. The N–S bond length of 1.5478(18) Å indicates double-bond character. Again, the S–O1 [1.5027(13) Å; formal S–O] and S–O2 [1.4412(15) Å; S=O] bond lengths differ significantly due to coordination to Ru. Coordination of the anionic oxygen donor induces desymmetrization of both the sulfur and ruthenium center. Interestingly, only one diastereoisomer is observed (Ru^{S}S^S and its enantiomer Ru^{R}S^R) in the racemic crystal structure as the complex crystallizes as a true racemate. In solution, the configuration of at least one of the two chiral centers is retained (on the NMR spectroscopic timescale), because the two phenyl groups on phosphorus showed distinct signals in the ^{13}C NMR spectrum. Piano-stool complexes with ligands **1B^H**, **1C^H**, and **1D^H** could be synthesized using this protocol, thus exemplifying the possibility to fine-tune such complexes with electron-donating (**7** and **8**) or -withdrawing groups (**9**) at sulfur.

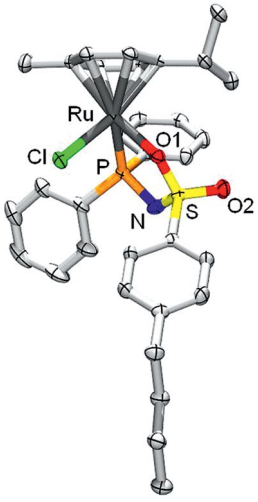


Figure 2. ORTEP plot (50% probability displacement ellipsoids) of piano-stool complex **6**, [RuCl(**1A**)(η^6-cymene)]. Hydrogen atoms and THF solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–P 2.3240(5), Ru–Cl 2.3943(5), Ru–O1 2.1419(14), P–N 1.651; O1–Ru–Cl 86.61(4), P–N–S 117.69(11), N–S–O1 111.29(9), N–S–O2 114.22(10), Ru–O1–S 121.48(8).

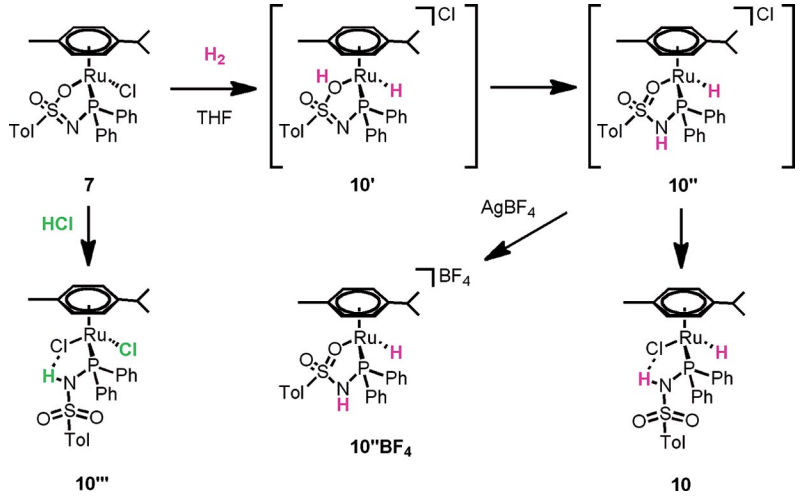
Heterolytic Splitting of Dihydrogen

In analogy to the activity displayed by Noyori's complex and related reversible amido-to-amino switchable ligands,[7] we were curious as to whether the combination of a Lewis acidic metal and a Brønsted basic ligand would result in direct heterolytic H_2 cleavage. It should be noted that there is a pronounced difference in both Ru–amide geometry (equatorial/meridional versus piano-stool) and Ru–amide character (inner-sphere coordination versus two-bond separation), which might have pronounced differences for amide protonolysis. When complex **7**, a close analogue of **6** that features ligand $\mathbf{1B^H}$, was kept under 5 bar of H_2 in [D_8]-THF, a doublet was obtained at δ = –8.34 ppm ($J_{P,H}$ = 52 Hz) in the ^{1}H NMR spectrum [33% conversion after 18 h on the basis of ^{31}P NMR spectroscopy: δ = 87.7 ppm ($J_{P,H}$ = 52 Hz)], which is strongly suggestive of heterolytic hydrogen splitting and reprotonation of the METAMORPhos ligand. Full conversion to the hydride complex could be reached at higher H_2 pressure, thereby allowing the isolation and full characterization of this stable compound. The corresponding expected –N*H* signal was observed at δ = 7.57 ppm, identified by its coupling with phosphorus ($J_{P,H}$ = 10.9 Hz). The addition of KPF_6 (1 equiv.) while applying H_2 pressure led to the same NMR spectroscopic features with no indication of the PF_6 anion (by ^{31}P and ^{19}F NMR spectroscopy). Hence, complex **10** is formulated as the neutral complex [Ru(H)(Cl)($\mathbf{7^H}$)]. This was evident from HRMS data (ESI: *m*/*z* 666.034 for [M + K] and 592.103 for [M – Cl]). We postulate that the Ru–Cl bond is sufficiently labilized in polar solvent (KPF_6 might further assist in labilizing the chloride ligand) to allow coordination of molecular hydrogen and its subsequent heterolytic cleavage. Presumably, initial interaction of the Ru–O bond with H_2 occurs, thus leading to the transient [Ru(H)(κ^2-O^H,*P*)] species **10′** that undergoes intramolecular proton shuttling to afford **10′′**, which bears the $\mathbf{P^{III}}$ tautomer within the Ru coordination sphere as neutral P,O chelate. The weakly coordinating oxygen of the protonated chelating ligand is then displaced by a chloride (KCl is partially soluble in THF) to give neutral complex **10** (Scheme 6). Addition of an excess amount of HCl (1 M solution in diethyl ether) to **7** also led to smooth reformation of the coordinated neutral $\mathbf{P^{III}}$ tautomer: the –N*H* signal was observed at δ = 6.68 ppm ($J_{P,H}$ = 11.0 Hz). By in situ chloride abstraction with $AgBF_4$ during the H_2-splitting process we were also able to identify the cationic complex $\mathbf{10''BF_4}$, which could be characterized in solution by ^{1}H and ^{31}P NMR spectroscopy. Interestingly, **10′′** was observed as an equimolar mixture of both diastereoisomers, with the Ru and S atoms as stereogenic centers.

Notably, the use of complex **9**, which bears the electron-poor bis(trifluoromethyl)phenyl sulfonamide derivative, neither resulted in full conversion nor in clean formation of a single hydridic species. After 18 h at 50 bar, two hydrides could be observed at δ = –7.26 ($J_{P,H}$ = 45 Hz) and –8.05 ppm ($J_{P,H}$ = 52 Hz) in a ratio of 1:8 and 1:1.7 with respect to the remaining starting complex, as well as a cymene species bearing no hydride. Although we did not characterize this mixture further, the incomplete conversion might indicate the establishment of an equilibrium with this particular system that features a more acidic METAMORPhos ligand. This not only supports the active involvement of the METAMORPhos framework in cleavage of the H–H bond, but also provides clear indications of the tunable character of this PNSO scaffold relative to other types of proton-responsive systems.

Substitution Reactions on Piano-Stool Complex 7

Recently, the group of Bruneau reported arene-free complexes based on a phosphinosulfonate ligand that were generated from similar piano-stool complexes as **6**–**9**.[17] Replacement of the cymene fragment by acetonitrile led to higher catalytic activity in the hydrogenation of ketones. Consequently, we were curious to establish similar substitution chemistry on piano-stool complexes bearing the related monoanionic METAMORPhos scaffold. Stirring complex **7** in acetonitrile with $NaPF_6$ for 2 days at room temperature



Scheme 6. Heterolytic activation of H_2 by piano-stool complex **7**.

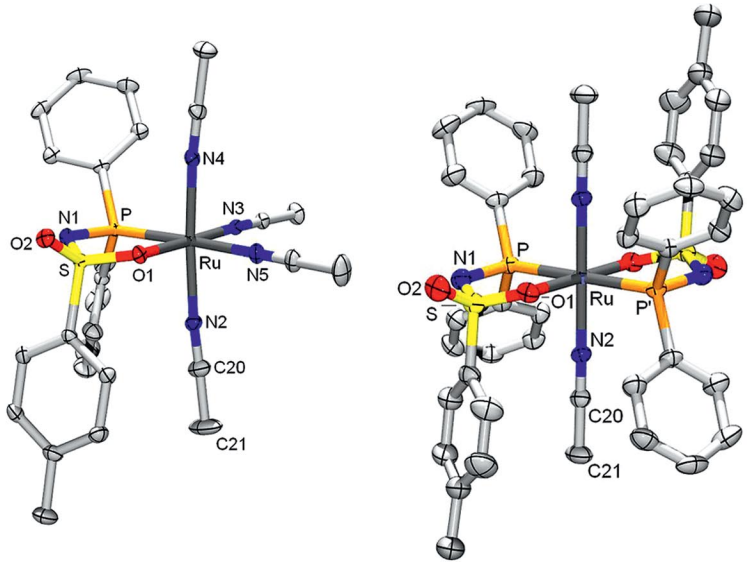


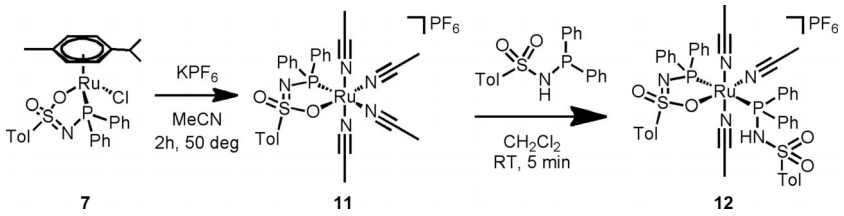
Figure 3. Solid-state structures of **11** (left) and **13** (right). Hydrogen atoms and PF_6 counterion and CH_2Cl_2 solvent (for **11**) have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **11**: Ru–P 2.2637(3), Ru–O1 2.1210(10), Ru–N2 2.0200(13), Ru–N3 1.9991(13), Ru–N4 2.0175(12), Ru–N5 2.1248(13), P–N1 1.6720(12), N1–S 1.5544(12), S–O1 1.4996(10), S–O2 1.4482(10); P–Ru–O1 83.87(3), P–Ru–N2 93.27(4), P–Ru–N3 96.87(4), P–Ru–N5 171.22(4), N2–Ru–N4 175.11(5), O1–Ru–N3 178.70(4), P–N1–S 116.65(7), N1–S–O1 112.65(6), N1–S–O2 112.05(6), Ru–O1–S 117.44(6), Ru–N2–C20 174.81(15). For **13**: Ru–P 2.3230(6), Ru–O1 2.1334(16), Ru–N2 2.0112(19), P–N1 1.671(2), N1–S 1.552(2), S–O1 1.4978(18), S–O2 1.4387(19); P–Ru–O1 81.31(5), P–Ru–N2 90.41(6), P′–Ru–O1 98.69(5), O1–Ru–N2 89.55(7), P–N1–S 115.40(13), N1–S–O1 113.36(11), N1–S–O2 113.00(12), Ru–O1–S 118.55(9). Symmetry operation *i*: 1 – *x*, 1 – *y*, 1 – *z*.

(or for one hour at 50°) yielded complex **11** in almost quantitative yield. ^{1}H NMR spectroscopy clearly illustrated complete dissociation of the cymene fragment after reaction, and the ^{31}P NMR spectrum showed only a singlet at δ = 73.5 ppm (and the PF_6 ion). X-ray crystal-structure analysis confirmed the displacement of the cymene ligand by four acetonitrile molecules as well as complete exchange of chloride for PF_6 (Figure 3, left). The Ru–N bond length varies from 1.9991(13) Å for the NCMe *trans* to the oxygen atom to 2.1248(13) Å for the NCMe *trans* to P, which follows the same trend as reported for related compounds.[17] There is slight out-of-plane bending of the two axial NCMe units away from the PNSO side, which might be related to slight steric hindrance [N2–Ru–N4 175.11(5) Å, Ru–N2–C20 174.81(15) Å].

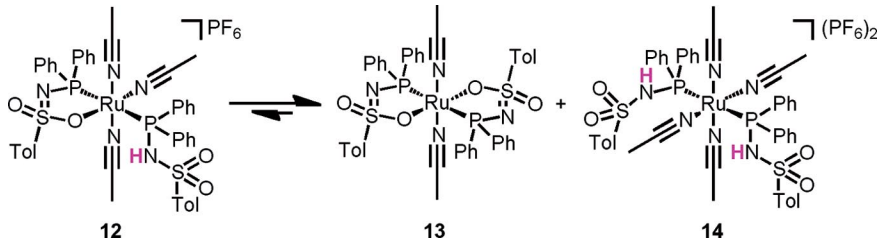
At least part of the weakly coordinated acetonitrile ligand set is easily displaced, as complex **11** reacted almost instantaneously at room temperature with one additional equivalent of **1B^H** to yield complex **12**, [Ru(**1B**)(**1B^H**)(NCMe)$_3$]PF_6 (Scheme 7). The exogenous METAMORPhos ligand remained protonated at nitrogen, because a doublet was observed in the ^{1}H NMR spectrum at δ = 6.96 ppm ($^2J_{P,H}$ = 15.1 Hz) for the –N*H* group. At room temperature, two doublets are detected in the ^{31}P NMR spectrum at δ = 74.2 and 70.8 ppm ($^2J_{P,H}$ = 15 Hz). The –NH group is potentially involved in intramolecular hydrogen bonding with the anionic oxygen donor of the P,O chelate between the two ligands, as previously suggested for analogous rhodium complexes.[10a] This is supported by the observation of coalescence using ^{31}P variable-temperature (VT) NMR spectroscopy, which indicates two equal P donors and consequently fast intramolecular proton shuttling. Single crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of methyl *tert*-butyl ether (MTBE) into a CH_2Cl_2 solution of **12**. Instead of the anticipated monocationic complex, the resulting molecular structure showed neutral complex **13**, which contained two deprotonated, anionic METAMORPhos ligands (Figure 3, right). The molecule is located on an exact, crystallographic inversion center and bears two axial NCMe ligands and two P,O chelates, with the strong O donors in a mutually *trans* configuration. The P–Ru–O1 angle is slightly smaller [81.31(5)°] than in parent species **11**.

We speculate that the formation of **13** originates from an autoprotonolysis process between two molecules of **12**, as depicted in Scheme 8, which results in formation of dication **14** and neutral species **13** that was characterized in the solid state. The proposed equilibrium might be influenced by solvent polarity, but this has not been further investigated to date. Only complex **12** could be detected by HRMS spectrometry.

Upon addition of phosphoramidite-based METAMORPhos derivative [HNEt$_3$][**1K**] (1 equiv.), which bears a chiral binaphthol auxiliary, to complex **11**, we observed the formation of two diastereomers (**15a** and **15b**) in the ^{31}P NMR spectrum due to the presence of a chiral sulfur atom as well as the atropisomeric chirality of the binaphthyl unit. This implies that the chirality at sulfur is kinetically stable under these ligand substitution conditions, which could hold promise as an additional ligand design element for applications in asymmetric catalysis. This is currently under investigation.



Scheme 7. Synthesis of cymene-free complex **11**, [Ru(**1B**)(NCMe)$_4$]PF$_6$, and derivative **12** bearing two METAMORPhos ligands.



Scheme 8. Proposed autoprotonolysis of **12** to generate neutral complex **13**, [Ru(**1B**)$_2$(NCMe)$_2$], and dicationic **14**.

Conclusion

In summary, we have successfully synthesized a range of METAMORPhos ligands by coupling sulfonamides with chlorophosphorus reagents. The introduction of electron-donating or -withdrawing substituents is possible at phosphorus and sulfur independently, thus creating a versatile library of these proton-responsive ligands. The presence of steric bulk at phosphorus strongly favors formation and isolation of METAMORPhos ligands over the diphosphorus (PPN) compound **2**, which results from double condensation. The prototropic behavior of the METAMORPhos ligand family is tuned by the electronic character of both P and S substituents, but to a varying extent. The use of dialkylchlorophosphines leads to exclusive formation of the **P^{V}** tautomer, which features a P–H unit, whereas for chlorodiarylphosphines the ratio between the **P^{III}** (N–H) and **P^{V}** (P–H) tautomers is strongly dependent on the nature of the organic group at sulfur. The coordination of these METAMORPhos ligands to ruthenium was investigated by using two different Ru precursors. The first piano-stool-type complexes with METAMORPhos ligands were prepared and fully characterized, including X-ray crystal-structure determination (for **6**). Exclusive coordination as the monoanionic P,O chelate was observed for a range of complexes in the solid state, whereas the corresponding solution phase also indicated coordination as neutral monodentate P donor. Upon coordination of the ligand platform as P,O chelate, the sulfur atom becomes chiral, and this chirality is retained during subsequent substitution reactions at Ru, as evidenced by the conversion of [Ru(**1B**)(NCMe)$_4$]PF$_6$. This feature was not observed for Rh–METAMORPhos complexes due to their dynamic coordination behavior. The heterolytic splitting of dihydrogen occurs in a bifunctional manner, thereby resulting in reprotonation of the anionic P,O chelate and formation of the neutral species [Ru(H)(Cl)(**L^{H}**)] with only P-coordination. Tuning of the proton-responsive character allows for modulation of the rate of H_2 splitting with these piano-stool Ru species. Current efforts focus on the utilization of these complexes with proton-responsive ligands in catalytic reactions and the potential exploitation of sulfur chirality for asymmetric transformations.

Experimental Section

Ligand 1E: Commercially available 3,5-bis(trifluoromethyl)phenyl sulfonamide (1 equiv., 10 mmol) was placed in a Schlenk flask under nitrogen. The compound was azeotropically dried with toluene and then dissolved in THF (15 mL) and triethylamine (25 mmol). A solution of bis(2-methylphenyl)chlorophosphine (10 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise under strong magnetic stirring at room temperature. After stirring overnight at 60 °C, the solution was filtered under a nitrogen atmosphere to remove the insoluble triethylamonium chloride salt. The solvent was removed under vacuum to leave a viscous oil. This residue was triturated with diethyl ether (50 mL) and subsequently filtered. After one day under dynamic vacuum, the oil solidified to yield a white solid that still contained triethylamine and traces of solvent (55% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.69–7.16 (aromatic region), 2.76 (q, $^{3}J_{H,H}$ = 7.3 Hz, CH_2 of NEt_3), 2.17 (s), 1.12 (t, $^{3}J_{H,H}$ = 7.3 Hz, CH_3 of NEt_3) ppm. **1E^{H}** to NEt_3 ratio of 5 based on proton integration. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ = 142.2 (s, C_{quat}), 142.0 (s, C_{quat}), 133.8 (s, CH), 133.0 (d, $J_{P,C}$ = 3 Hz, CH), 132.9 (s, CH), 132.8 (s, CH), 132.7 (s, C_{quat}), 132.4 (s, C_{quat}), 132.0 (s, C_{quat}), 131.9 (br. s, CH), 131.4 (d, $J_{P,C}$ = 3 Hz, CH), 127.1 (br. m, CH), 124.9 (br. m, CH), 124.7 (s, C_{quat}), 122.0 (s, C_{quat}), 20.6 (s, CH_3), 20.4 (s, CH_3) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ = –63.2 (s) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 9.5 (s, **P^{III}** tautomer), 1.0 (d, $^{1}J_{P,H}$ = 497 Hz, **P^{V}** tautomer) ppm. **P^{III}** is the major component, on ^{31}P integration. HRMS (ESI+): *m*/*z* calcd. for $C_{28}H_{34}F_6N_2O_2PS$ (NEt_3 adduct): $[M + HNEt_3]^+$: 607.19828; found 607.19790.

Ligand 1F: Obtained by means of the same procedure as compound **1B**, starting from commercially available chlorodiisopropylphosphine and *p*-butylphenyl sulfonamide in 75% yield. ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 7.82 (d, $^3J_{H,H}$ = 8 Hz, 2 H), 7.21 (d, $^3J_{H,H}$ = 8 Hz, 2 H), 6.36 (dt, $^1J_{H,P}$ = 441, $^2J_{H,H}$ = 4 Hz, 1 H, P*H*), 2.63 (t, $^3J_{H,H}$ = 7 Hz, 2 H, Ar–*CH*$_2$–CH$_2$–CH$_2$–CH$_3$), 2.23 (m, 2 H, CH isopropyl), 1.58 (m, 2 H, Ar–CH$_2$–*CH*$_2$–CH$_2$–CH$_3$), 1.33 (m, 2 H, Ar–CH$_2$–CH$_2$–*CH*$_2$–CH$_3$), 1.24 (m, 12 H, CH$_3$ isopropyl), 0.91 (t, $^3J_{H,H}$ = 7 Hz, 3 H, Ar–CH$_2$–CH$_2$–CH$_2$–*CH*$_3$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 145.8 (s), 142.9 (s), 128.2 (s), 125.6 (s), 34.2 (d, $^1J_{P,C}$ = 211 Hz), 23.8 (s), 23.1 (s), 22.1 (s), 16.4 (s), 15.4 (d, $^2J_{P,C}$ = 4 Hz), 13.8 (s) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.9 (m, $^1J_{H,P}$ = 441 Hz) ppm.

Synthesis of 3 (mixture of diastereoisomers): Ligand **1F** (1 equiv., 0.15 mmol) and [Ru(H)(Cl)(PPh$_3$)$_3$(CO)] (1 equiv., 0.15 mmol) were heated at reflux overnight in toluene (5 mL) under nitrogen. The solvent was removed by vacuum and the residue was dissolved in diethyl ether (2 mL). Hexane (8 mL) was added and the solution was kept at –20 °C overnight, thus leading to a yellow precipitate that was filtered and washed with hexane (10 mL). Complex **3** was obtained in 35% yield. Slow evaporation of a saturated solution of complex **3** in diethyl ether resulted in the formation of yellow crystals suitable for X-ray analysis after one week at room temp. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.21–6.94 (aromatic region, 38 H), 2.71–2.53 (4 H, Ar–*CH*$_2$–CH$_2$–CH$_2$–CH$_3$ both diastereoisomers), 2.20–2.02 (alkyl region, 2 H), 1.67–0.67 (alkyl region, 42 H) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 100.0 (d, $^2J_{P,P}$ = 25.5 Hz, diastereoisomer a), 97.7 (d, $^2J_{P,P}$ = 24.0 Hz, diastereoisomer b), 39.1 (d, $^2J_{P,P}$ = 24.0 Hz, diastereoisomer b), 37.4 (d, $^2J_{P,P}$ = 25.5 Hz, diastereoisomer a) ppm. Ratio of diastereoisomer a/b = 1.7 After purification, based on ^{31}P integrals. HRMS (ESI+): *m*/*z* calcd. for $C_{70}H_{86}Cl_2N_2O_6P_4Ru_2S_2$: 1512.23418 $[M^{\cdot}]^+$; found 1512.23667.

General Synthesis of Piano-Stool Complexes: Ligand **1** (2 mmol, 1 equiv.) and [{RuCl(cymene)(μ-Cl)}$_2$] (2 mmol, 1 equiv.) were dissolved in THF (20 mL) at room temperature. Triethylamine (1 mL) was added, and the solution was stirred at room temperature for 2 h. The solution was filtered, and the THF was evaporated. The residue was dissolved in dichloromethane (5 mL) and diethyl ether (35 mL) was added dropwise, thus leading to an orange precipitate. The precipitate was filtered and washed with diethyl ether (10 mL).

Complex 6: Obtained in 93% yield from ligand **1A**. For crystallization, a solution of **6** (20 mg) in THF (0.2 mL) was layered with diethyl ether (1 mL) to give a red crystalline material (suitable for X-ray analysis) after two weeks of slow diffusion at room temp. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.36 (12 H), 7.08 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH), 5.68 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, Ar$_{cymene}$ CH), 5.40 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, Ar$_{cymene}$ CH), 5.26 (m, $^3J_{H,H}$ = 5.8 Hz, 1 H, Ar$_{cymene}$ CH), 4.83 (m, $^3J_{H,H}$ = 5.7 Hz, 1 H, Ar$_{cymene}$ CH), 2.59 (m, 1 H, *i*Pr$_{Cymene}$ CH), 2.54 [t, $^3J_{H,H}$ = 7.0 Hz, 2 H, Ar–*CH*$_2$–(CH$_2$)$_2$–CH$_3$], 2.12 (s, 3 H, CH$_{3\ cymene}$), 1.50 (m, 2 H, Ar–CH$_2$–*CH*$_2$–CH$_2$–CH$_3$), 1.32–1.18 [8 H, isopropyl cymene CH$_3$ and Ar–(CH$_2$)$_2$–*CH*$_2$–CH$_3$] 0.87 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, butyl CH$_3$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 146.7 (s, C$_{quat}$, butylphenyl), 142.2 (d, $^1J_{P,C}$ = 60.0 Hz, C$_{quat}$, phenyl), 139.1 (d, $^3J_{P,C}$ = 3.6 Hz, C$_{quat}$, butylphenyl), 133.1 (d, $^1J_{P,C}$ = 67.3 Hz, C$_{quat}$, phenyl), 132.2 (d, $J_{P,C}$ = 11.3 Hz, CH, phenyl), 130.627 (d, $J_{P,C}$ = 2.7 Hz, CH, phenyl), 130.4 (d, $J_{P,C}$ = 11.4 Hz, CH, phenyl), 130.047 (d, $J_{P,C}$ = 2.8 Hz, CH, phenyl), 128.7 (d, $J_{P,C}$ = 10.8 Hz, CH, phenyl), 128.7 (s, CH, butylphenyl), 128.0 (d, $J_{P,C}$ = 11.8 Hz, CH, phenyl), 127.9 (s, CH, butylphenyl), 105.090 (s, C$_{quat}$, cymene), 94.614 (d, $^2J_{P,C}$ = 6.2 Hz, CH, cymene), 93.4 (s, C$_{quat}$, cymene), 86.5 (d, $^2J_{P,C}$ = 6.9 Hz, CH, cymene), 86.0 (d, $^2J_{P,C}$ = 3.2 Hz, CH, cymene), 83.2 (d, $^2J_{P,C}$ = 3.2 Hz, CH, cymene), 35.6 (s, CH$_2$, butyl), 33.4 (s, CH$_2$, butyl), 30.7 (s, CH, cymene), 22.4 (s, CH$_3$, CH$_3$–CH cymene), 22.3 (s, CH$_2$, butyl), 22.3 (s, CH$_3$, CH$_3$–CH cymene), 18.7 (s, CH$_3$, CH$_3$–Ar cymene), 14.0 (s, CH$_3$, butyl) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 73.5 (s) ppm. HRMS (FAB+): *m*/*z* calcd. for $C_{32}H_{38}ClNO_2PRuS$: 668.1093 $[M + H]^+$; found 668.1097.

Complex 7: Obtained in 98% yield from ligand **1B**. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.82–7.39 (aromatic region, 12 H), 7.11 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, tolyl aromatic CH), 5.70 (m, $^3J_{H,H}$ = 6.3 Hz, 1 H, Ar$_{cymene}$ CH), 5.42 (d.m., $^3J_{H,H}$ = 6.3 Hz, 1 H, Ar$_{cymene}$ CH), 5.230 (d.m., $^3J_{H,H}$ = 5.8 Hz, 1 H, Ar$_{cymene}$ CH), 4.80 (m, $^3J_{H,H}$ = 5.8 Hz, 1 H, Ar$_{cymene}$ CH), 2.49 (m, 1 H, isopropyl cymene CH), 2.31 (s, 3 H), 2.07 (s, 3 H), 1.24 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, isopropyl CH$_3$), 1.16 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, isopropyl CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 73.3 (s) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 142.5 (d, $^1J_{P,C}$ = 59.5 Hz, C$_{quat}$, phenyl), 142.4 (s, C$_{quat}$, tolyl C–Me), 140.0 (d, $^3J_{P,C}$ = 3.7 Hz, C$_{quat}$, C–S), 134.0 (d, $^1J_{P,C}$ = 67.4 Hz, C$_{quat}$, phenyl), 132.4 (d, $J_{P,C}$ = 11.2 Hz, CH, phenyl), 130.9 (d, $J_{P,C}$ = 2.9 Hz, CH, phenyl), 130.6 (d, $J_{P,C}$ = 11.2 Hz, CH, phenyl), 130.4 (d, $J_{P,C}$ = 2.7 Hz, CH, phenyl), 129.3 (s, CH, tolyl), 129.1 (d, $J_{P,C}$ = 10.9 Hz, CH, phenyl), 128.4 (d, $J_{P,C}$ = 11.7 Hz, CH, phenyl), 127.9 (s, CH, tolyl), 105.7 (s, C$_{quat}$, cymene), 95.3 (d, $^2J_{P,C}$ = 6.3 Hz, CH, cymene), 94.0 (s, C$_{quat}$, cymene), 86.9 (d, $^2J_{P,C}$ = 6.9 Hz, CH, cymene), 86.1 (d, $^2J_{P,C}$ = 3.3 Hz, CH, cymene), 82.6 (d, $^2J_{P,C}$ = 2.9 Hz, CH, cymene), 31.1 (s, CH, cymene), 22.6 (s, CH$_3$), 22.2 (s, CH$_3$), 21.6 (s, CH$_3$), 18.8 (s, CH$_3$, CH$_3$–Ar cymene) ppm. HRMS (ESI+): *m*/*z* calcd. for $C_{29}H_{32}ClNO_2PRuS$: 626.06234 $[M + H]^+$; found 626.06409.

Heterolytic Cleavage of H_2 Using 7 to Yield Complex 10: *Method A*: Complex **7** (1 equiv., 12.5 μmol), KPF_6 (10 equiv., 125 μmol), and [D$_8$]THF (0.5 mL) were charged in a high-pressure NMR spectroscopy tube. The tube was pressurized with hydrogen (10 bar), stirred, and sonicated for 4 days. ^1H NMR (400 MHz, [D$_8$]THF): δ = 7.94 (m, 2 H, phenyl C–H), 7.85 (d, $^3J_{P,H}$ = 10.7 Hz, 1 H, N–H), 7.79 (m, 2 H, phenyl C–H), 7.42–7.32 (6 H, phenyl C–H), 6.96 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, tolyl C–H), 6.89 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, tolyl C–H), 5.63 (d, $J_{H,H}$ = 6.2 Hz, 1 H, Ar$_{cymene}$ C–H), 5.39 (d, $J_{H,H}$ = 5.8 Hz, 1 H, Ar$_{cymene}$ C–H), 4.72 (d, $J_{H,H}$ = 6.2 Hz, 1 H, Ar$_{cymene}$ C–H), 4.54 (s, dissolved H_2), 4.39 (d, $J_{H,H}$ = 5.8 Hz, 1 H, Ar$_{cymene}$ C–H), 2.25 (s, 3 H), 1.84 (m, 1 H, isopropyl cymene C–H), 1.80 (s, 3 H), 0.98 (d, $^3J_{H,H}$ = 5.0 Hz, 3 H, isopropyl cymene CH$_3$), 0.96 (d, $^3J_{H,H}$ = 5.0 Hz, 3 H, isopropyl cymene CH$_3$), –8.34 (d, J = 52.5 Hz, 1 H) ppm. ^{31}P NMR (162 MHz, [D$_8$]THF): δ = 87.7 (m, $J_{P,H}$ = 52 Hz) ppm. *Method B*: Complex **7** (1 equiv., 125 μmol) and KPF_6 (2 equiv., 250 μmol) were suspended in THF (2 mL). The solution was charged into an autoclave and submitted to H_2 (50 bar) for 10 h. After depressurizing to ambient conditions, the solution was filtered and the solvent was evaporated. The residue was dissolved in dichloromethane and filtered with an HPLC filter. The solvent was evaporated to yield complex **10** in quantitative yield. *Method C*: Complex **7** (1 equiv., 12.5 μmol) was dissolved in THF (0.5 mL) and submitted to an atmosphere of H_2 (50 bar) in an autoclave/NMR spectroscopy tube for 10 h. After depressurizing to ambient conditions, the solvent was evaporated to yield complex **10** in quantitative yield. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.92 (dd, $J_{P,H}$ = 11.5, $J_{H,H}$ = 7.5 Hz, 2 H, phenyl C–H), 7.76 (dd, $J_{P,H}$ = 12.0, $J_{H,H}$ = 7.1 Hz, 2 H, phenyl C–H), 7.57 (d, $^2J_{P,H}$ = 10.9 Hz, 1 H, N–H), 7.48–7.35 (6 H), 6.96 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, tolyl C–H), 6.91 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, tolyl C–H), 5.61 (d, $J_{H,H}$ = 6.2 Hz, 1 H, Ar$_{cymene}$ C–H), 5.36 (d, $J_{H,H}$ = 5.9 Hz, 1 H, Ar$_{cymene}$ C–H), 4.69 (d, $J_{H,H}$ = 6.2 Hz, 1 H, Ar$_{cymene}$ C–H), 4.28 (d, J = 5.8 Hz, 1 H, Ar$_{cymene}$ C–H), 2.28 (s, 3 H), 1.83 (s, 3 H), 1.81 (m, 1 H, isopropyl cymene C–H), 0.99 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H), –8.45 (d, $^2J_{P,H}$ = 52.0 Hz, 1 H) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 89.2 (m, $^2J_{P,H}$ = 52.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 143.1 (s, C$_{quat}$, tolyl C–Me), 139.5 (s, C$_{quat}$, tolyl C–Me), 136.0

(d, $^{1}J_{P,C}$ = 44.3 Hz, C_{quat}, phenyl), 135.2 (d, $^{1}J_{P,C}$ = 65.3 Hz, C_{quat}, phenyl), 133.6 (d, $J_{P,C}$ = 13.1 Hz, CH, phenyl), 133.1 (d, $J_{P,C}$ = 12.5 Hz, CH, phenyl), 131.4 (d, $J_{P,C}$ = 2.2 Hz, CH, phenyl), 131.1 (d, $J_{P,C}$ = 2.5 Hz, CH, phenyl), 129.4 (s, CH, tolyl), 128.4 (d, $J_{P,C}$ = 5.7 Hz, CH, phenyl), 128.2 (d, $J_{P,C}$ = 6.3 Hz, CH, phenyl), 126.4 (s, CH, tolyl), 110.0 (s, C_{quat}, cymene), 103.2 (s, C_{quat}, cymene), 93.2 (d, $^{2}J_{P,C}$ = 3.8 Hz, CH, cymene), 90.5 (d, $^{2}J_{P,C}$ = 6.6 Hz, CH, cymene), 89.10 (d, $^{2}J_{P,C}$ = 5.5 Hz, CH, cymene), 82.40 (d, $^{2}J_{P,C}$ = 3.0 Hz, CH, cymene), 31.4 (s, CH, cymene), 24.6 (s, CH_3), 22.0 (s, CH_3), 21.7 (s, CH_3), 19.0 (s, CH_3, CH_3–Ar cymene) ppm. HRMS (ESI+): *m/z* calcd. for $C_{29}H_{33}ClKNO_2PRuS$: 666.03425 $[M + K]^+$; found 666.03437; *m/z* calcd. for $C_{29}H_{33}NO_2PRuS$: 592.10203 $[M – Cl]^+$; found 592.10311.

In Situ Synthesis and Characterization of Complex 10′′: Complex **10** (1 equiv., 17.5 μmol), $AgBF_4$ (17.5 μmol), and CD_2Cl_2 (0.7 mL) were stirred for 2 h under nitrogen. The solution was filtered and introduced into a screw-cap NMR spectroscopy tube for direct measurement (^{31}P yield: 87.5%). ^{1}H NMR (500 MHz, MHz, CD_2Cl_2): δ = 7.88–7.24, 6.40 (br., Ar_{cymene} C–H), 6.33 (d, J = 4.5 Hz, Ar_{cymene} C–H), 6.26 (d, J = 6.0 Hz, Ar_{cymene} C–H), 6.18 (br., Ar_{cymene} C–H), 6.11 (br., Ar_{cymene} C–H), 5.82 (br., Ar_{cymene} C–H), 5.68 (d, J = 6.5 Hz, Ar_{cymene} C–H), 5.52 (br., Ar_{cymene} C–H), 2.50–0.09 (alkyl region), –9.06 (d, $^{2}J_{P,H}$ = 37.8 Hz), –9.16 (d, $^{2}J_{P,H}$ = 35.1 Hz) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2): δ = 100.4, 97.1 ppm. Complex **10′′** was formed as a 1:1 mixture of diastereoisomers (the eight cymene signals and both hydride signals integrate for 1H each; both phosphorus signals integrate for 1P). The phosphorus–hydride coupling was not observed in the ^{31}P NMR spectra due to broadened signals.

Complex 11: Complex **7** (1 equiv., 0.8 mmol) and KPF_6 (1.05 equiv., 0.84 mmol) were suspended in acetonitrile (50 mL). The reaction mixture was stirred for 2 h at 50 °C. The solvent was removed under vacuum, and the residue dissolved in dichloromethane (5 mL). The solution was filtered through an HPLC filter and dried. The residue was dissolved in dichloromethane (1 mL), and diethyl ether (10 mL) was added dropwise while stirring, thus leading to a pale yellow precipitate that was filtered and washed with diethyl ether (10 mL). Complex **11** was obtained in quantitative yield. For crystallization, a solution of **11** (17.5 μmol) in CD_2Cl_2 (0.7 mL) was filtered with an HPLC filter and layered with methyl *tert*-butyl ether (1 mL) to result in pale yellow crystals after two weeks of slow diffusion at room temp. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.82–7.73 (4 H), 7.59 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2 H, tolyl), 7.51–7.40 (6 H), 7.17 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2 H, tolyl), 2.59 (s, 3 H), 2.51 (s, 3 H), 2.35 (s, 3 H), 1.98 (s, 3 H), 1.77 (s, 3 H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ = 142.3 (s, C_{quat}, tolyl), 142.2 (d, $^{3}J_{P,C}$ = 3.7 Hz, C_{quat}, tolyl), 138.6 (d, $^{1}J_{P,C}$ = 62.8 Hz, C_{quat}, phenyl), 136.4 (d, $^{1}J_{P,C}$ = 61.2 Hz, C_{quat}, phenyl), 131.2 (d, $J_{P,C}$ = 11.6 Hz, CH, phenyl), 131.0 (d, $J_{P,C}$ = 2.5 Hz, CH, phenyl), 130.5 (d, $J_{P,C}$ = 11.7 Hz, CH, phenyl), 130.3 (d, $J_{P,C}$ = 2.9 Hz, CH, phenyl), 129.5 (s, CH, tolyl), 129.1 (d, $J_{P,C}$ = 11.1 Hz, CH, phenyl), 128.9 (d, $J_{P,C}$ = 11.0 Hz, CH, phenyl), 127.8 (s, C_{quat}, $NCCH_3$), 126.5 (s, CH, tolyl), 125.1 (s, C_{quat}, $NCCH_3$), 124.3 (s, C_{quat}, $NCCH_3$), 122.6 (d, $^{3}J_{P,C}$ = 15.4 Hz, C_{quat}, $NCCH_3$), 20.8 (s, CH_3, tolyl), 4.0 (s, CH_3, $NCCH_3$), 3.3 (s, CH_3, $NCCH_3$), 3.1 (s, CH_3, $NCCH_3$), 2.7 (s, CH_3, $NCCH_3$) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ = 87.5 (s), –142.3 (PF_6) ppm. HRMS (ESI+): *m/z* calcd. for $C_{27}H_{29}N_5O_2PRuS$: 620.08296 $[M + H]^+$; found 620.08594.

Complex 12: Complex **11** (1 equiv., 20 μmol) and ligand **1B** (20 μmol) were dissolved in dichloromethane (1 mL). The solution was stirred for 5 min at room temperature, and the solvent was evaporated. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.93–6.96 (28 H), 6.96 (dd, $^{2}J_{P,H}$ = 15.1, $^{4}J_{P,H}$ = 3.4 Hz, 1 H, N–H), 2.39 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ = 144.2 (s, C_{quat}, tolyl), 142.8 (d, $^{3}J_{P,C}$ = 2.7 Hz, C_{quat}, tolyl), 142.5 (s, C_{quat}, tolyl), 139.2 (s, C_{quat}, tolyl), 137.9 (dd, $^{1}J_{P,C}$ = 48.0, $^{3}J_{P,C}$ = 9.7 Hz, C_{quat}, phenyl), 135.5 (dd, $^{1}J_{P,C}$ = 47.6, $^{3}J_{P,C}$ = 10.3 Hz, C_{quat}, phenyl), 134.0 (dd, $^{2}J_{P,C}$ = 11.9, $^{4}J_{P,C}$ = 2.3 Hz, CH, phenyl), 133.5 (dd, $^{2}J_{P,C}$ = 11.7, $^{4}J_{P,C}$ = 2.2 Hz, CH, phenyl), 132.0 (br. d, $J_{P,C}$ = 12.1 Hz, CH, phenyl), 131.6 (dd, $^{2}J_{P,C}$ = 11.3, $^{4}J_{P,C}$ = 2.8 Hz, CH, phenyl), 131.3 (br. d, $J_{P,C}$ = 1.2 Hz, CH, phenyl), 130.5–130.4 (br., CH, overlapping signals), 129.9 (s, C_{quat}, $NCCH_3$), 129.7 (s, CH, tolyl), 129.5 (s, CH, tolyl), 129.4 (d, $J_{P,C}$ = 10.7 Hz, CH, phenyl), 129.1 (d, $J_{P,C}$ = 9.9 Hz, CH, phenyl), 128.9 (d, $J_{P,C}$ = 10.3 Hz, CH, phenyl), 128.6 (dd, $^{1}J_{P,C}$ = 14.2, $^{3}J_{P,C}$ = 7.1 Hz, C_{quat}, phenyl), 128.9 (d, $J_{P,C}$ = 10.1 Hz, CH, phenyl), 128.1 (d, $^{1}J_{P,C}$ = 7.1 Hz, C_{quat}, phenyl), 127.3 (s, C_{quat}, $NCCH_3$), 126.5 (s, CH, tolyl), 126.2 (s, CH, tolyl), 126.1 (s, C_{quat}, $NCCH_3$), 21.7 (s, CH_3, tolyl), 21.6 (s, CH_3, tolyl), 4.7 (s, CH_3, $NCCH_3$), 3.5 (s, CH_3, $NCCH_3$), 2.9 (s, CH_3, $NCCH_3$) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ = 74.2 (d, $^{2}J_{P,P}$ = 342 Hz), 70.8 (d, $^{2}J_{P,P}$ = 342 Hz), –146.7 (PF_6) ppm. HRMS (ESI+): *m/z* calcd. for $C_{44}H_{44}N_5O_4P_2RuS_2$: 934.13640 $[M – PF_6]^+$; found 934.13248.

CCDC-960163 (for **3**), -960164 (for **6**), -960165 (for **11**), and -960166 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental details, full characterization of all ligands and complexes, crystallographic data, NMR spectra.

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