The role of METAMORPhos ligands in transition metal complex formation and catalysis
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Chapter 6

Bifunctional Reactivity of Rh and Ir METAMORPhos Piano-Stool Complexes
6.1 Introduction

Outer sphere ligand-substrate interactions are becoming more prominent in the field of homogeneous catalysis. By applying bifunctional ligands, making use of for instance hydrogen bond interactions or acid-base reactivity, catalyst activity and selectivity can be steered, opening up new directions for reactivity.[1] Among the most well-known examples of bifunctional ligands applied in catalysis is Noyori’s ruthenium-diamine, which is employed in the (transfer)-hydrogenation of C=O and C=N bonds, see Figure 1a. This catalyst contains a bifunctional (NH) group in the α-position to the metal, which is involved in proton transfer and hydrogen bond formation during catalysis.[2] The iridium and rhodium analogues of this catalytic system are also reported to be excellent catalysts for the hydrogenation of C=O and C=N bonds.[3]

Other than Noyori’s ruthenium-diamine catalysts, examples are known where the ligand bifunctional group is not directly connected to the metal (i.e. in the α-position) for instance: Shvo’s bridged-diruthenium complexes (bifunctional OH group)[4] and Milstein’s ruthenium PNN pincer complexes (bifunctional CH group),[5] see Figure 1b and 1c respectively. These catalysts have successfully been applied in (transfer)-hydrogenation of C=O and C=N bonds and dehydrogenative coupling reactions.[3-4] Inspired by the advances in catalysis obtained with these complexes, the search for novel bifunctional ligands is a rapidly evolving field of research.

Figure 1. Catalysts employed by Noyori (a), Shvo (b) and Milstein (c) and a METAMORPhos-Ir/Rh piano-stool complex wherein the ligand is anionic and P,O coordinated (d).

The family of METAMORPhos ligands (which are based on a -PNSO₂- backbone) has been shown to combine various bifunctional properties.[6] This type of ligand bears a hydrogen bonding moiety (-NHSO₂) in proximity to a phosphorus donor and also displays proton responsive properties. Previous insights concerning the reactivity of METAMORPhos-type ligands with iridium encouraged an investigation into the potential bifunctional reactivity of METAMORPhos based piano-stool complexes of rhodium and iridium.[6a, 6b, 6e, 6g] It is envisioned that deprotonation of METAMORPhos, that is coordinated to a Rh^{III} or Ir^{III}-center, could generate P,O-chelate piano-stool complexes containing two potential bifunctional sites.
(an oxygen α to the metal and a nitrogen β to the metal, see Figure 1d). These complexes can operate via new reaction pathways involving bifunctional substrate activation.

6.2 Results and discussion

6.2.1 Preparation and characterization of Ir- and Rh-METAMORPhos piano-stool complexes

Mixing one equivalent of ligand 1 with 0.5 equivalent [Cp*IrCl₂]₂ in CD₂Cl₂ instantly led to complete consumption of the starting materials and formation of a single species, which was characterized by multinuclear NMR spectroscopy. In the ³¹P{¹H} NMR spectrum the formed complex displayed a singlet at 37.57 ppm. The signals of the Cp* ligand appeared as doublets in the ¹H NMR spectrum due to coupling with phosphorus (J₉-P = 2.4 Hz), which is a clear indication of P-coordination to the iridium center. The NH resonance of the METAMORPhos ligand (5.53 ppm in the free ligand) was shifted downfield to 7.39 ppm. Based on these observations, the complex is formulated as neutral P-coordinated METAMORPhos complex 2a (see Scheme 1), which was found to be in agreement with HR-MS and X-ray diffraction analyses. Crystals of complex 2a suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a concentrated CH₂Cl₂ solution of 2a. The molecular structure confirms monodentate coordination via the P donor of the neutral METAMORPhos ligand, see Scheme 1 for molecular structure of 2a. A hydrogen bond interaction between the N-H of the METAMORPhos ligand and the chloride ligands Cl₁ and Cl₂ was observed [N₁⋯Cl₁ 3.1452(14), N₁⋯Cl₂ 3.2531(14)]. Previously reported intramolecular N⋯Cl distances for complexes containing similar secondary N-H⋯Cl interactions are in agreement with distances observed. The rhodium analogue (2b) of complex 2a, was prepared with [Cp*RhCl₂]₂ as metal precursor under the same reaction conditions. Complex 2b displayed a doublet at 67.58 ppm (J₉-Rh = 151.7 Hz) in the ³¹P{¹H} NMR and displayed same characteristic features as 2a in ¹H NMR.

The coordination behavior of the METAMORPhos ligand in these complexes was further studied in the presence of base. Stirring 2a in a suspension of sodium acetate (NaOAc) in CH₂Cl₂ at room temperature led to the clean formation of a novel complex (3a), concomitant with the formation of HOAc and the precipitation of NaCl, see Scheme 2. The reaction was monitored by ³¹P{¹H} NMR spectroscopy; the disappearance of 2a coincides with the appearance of a singlet at 48.80 ppm. Phosphorus coordination of the ligand in 3a could be confirmed by ¹H NMR spectroscopy, as a coupling of the Cp* ligand to phosphorus was observed (Jₜ-P = 2.1 Hz). In complex 3a the METAMORPhos ligand is proposed to be deprotonated and coordinated as P,O-chelate, as no NH resonance was observed in the ¹H NMR spectrum. Similar reactivity of complex 2b with NaOAc was observed and led to the formation of rhodium analogue complex 3b (see Scheme 2).

Scheme 2. Deprotonation of 2a-b with NaOAc generates P,O-coordinated complexes 3a-b, wherein the ligand is P,O-bound in an anionic fashion.
Crystals suitable for X-ray diffraction analysis for both 3a and 3b were obtained by slow diffusion of pentane into a CH$_2$Cl$_2$ solution saturated with 3a and 3b, respectively. The molecular structures confirmed the anticipated P,O-coordination of the ligand in both complexes, see Figure 2a and 2b for the isostructural molecular structures of complex 3a and 3b. Compared to the bond lengths found in the precursor species 2a, shorter N-S bond lengths [1.5465(13) Å and 1.5495(12) Å] were found, together with an elongated S-O$_1$ bond [1.5096(12) Å and 1.5010(11) Å] for 3a and 3b, respectively. This clearly shows that the ligand in complexes 3a-b is deprotonated.

Attempts to deprotonate complex 2a with other bases such as NEt$_3$ or DBU (1,8-diazabicyclo-undec-7-ene) were less successful. Using an excess of NEt$_3$ or DBU as a base in THF or CH$_2$Cl$_2$ did generate a signal in the $^{31}$P{$_1$H} NMR spectrum indicative of formation of 3a, concomitant with upfield chemical shifts for the signals of NEt$_3$ or DBU, which suggests the formation of amine-HCl salts as by-product. However, these salts could not be separated by precipitation and upon addition of pentane, complex 2a was recovered.

![Figure 2a. Molecular structure of 3a, blue: Ir, green: Cl, orange: P, purple: N, yellow: S, red: O. Selected bond lengths in Å: Ir$_1$–P$_1$ 2.2967(5), Ir$_1$–O$_1$ 2.1632(11), Ir$_1$–Cl$_1$ 2.3982(6), P$_1$–N$_1$ 1.6536(13), N$_1$–S$_1$ 1.5465(13), S$_1$–O$_1$ 1.5096(12), S$_1$–O$_2$ 1.4448(13). Selected bond angle (°): P$_1$–Ir$_1$–O$_1$ 80.41(3).](image)

![Figure 2b. Molecular structure of 3b, blue: Ir, green: Cl, orange: P, purple: N, yellow: S, red: O. Selected bond lengths in Å: Rh$_1$–P$_1$ 2.3085(4), Rh$_1$–O$_1$ 2.1667(11), Rh$_1$–Cl$_1$ 2.3983(4), P$_1$–N$_1$ 1.6472(12), N$_1$–S$_1$ 1.5495(12), S$_1$–O$_1$ 1.5010(11), S$_1$–O$_2$ 1.4457(12). Selected bond angle (°): P$_1$–Ir$_1$–O$_1$ 80.42(3).](image)
6.2.2 Bifunctional activation of H₂ by complexes 3a-b

Complexes 3a-b were studied in the activation of H₂ to investigate whether the ligand shows any propensity to facilitate heterolytic cleavage. When complex 3a was dissolved in CD₂Cl₂ and pressurized with H₂ (5 bar) at room temperature, no changes were observed in either the ¹H or the ³¹P{¹H} NMR spectrum. Upon heating the reaction mixture for 16 hours at 40 °C, a signal corresponding to an Ir-hydride (a doublet at -14.0 ppm) was observed in minor concentrations (approximately 5% conversion). Fortunately, pressurizing 3a with H₂ (5 bar) in THF instantly led to the clean formation of a single Ir-hydride species 4a (see Scheme 3). A singlet at 40.98 ppm was observed in the ³¹P{¹H} NMR spectrum and the hydride signal appears as a doublet at -14.0 ppm (J₉₁₇ = 39.1 Hz) in the ¹H NMR spectrum due to coupling with phosphorus.[⁹] The N-H resonance of 4a was found to overlap with a multiplet at 7.86-7.73 ppm. The formation of 4a is proposed to proceed via several steps: 1) dissociation of the chloride ligand to generate a cationic iridium complex containing a vacant site, 2) heterolytic cleavage of H₂ over the Ir-O bond to give intermediate 4a', 3) O-H to N-H proton shuttling and chloride re-coordination to form 4a (see Scheme 3). Chloride decoordination is likely more facile in THF-d₈ as the generated cationic Ir<sup>III</sup> 16e complex contains a vacant site that can be stabilized by solvent coordination. Dichloromethane (CH₂Cl₂) is a much weaker coordinating solvent than THF, which can explain the slow formation of 4a in CH₂Cl₂. In agreement with this, when complex 3a is first treated with NaBARF in order to abstract the chloride ligand and subsequently pressurized with H₂ (5 bar), the formation of an Ir-hydride species is instantaneous, also in CD₂Cl₂. As complex 4a was indeed found to facilitate the heterolytic cleavage of H₂, this species was investigated in the catalytic hydrogenation of acetophenone. Using 5 mol% of 3a in THF and applying 5 bar of H₂, in situ formed 4a was detected by ¹H NMR spectroscopy but no conversion of acetophenone to 1-phenylethan-1-ol was observed after 16 hours at 60 °C. The lack of activity of complex 4a can be explained by 1) decreased acidity of the N-H group in the ligand upon rearrangement from P,O- to P-coordination (3a to 4a), hampering protonation of the ketone and/or 2) inhibitory formation of an intramolecular N-H···Cl hydrogen bond, which hinders proton transfer to the ketone.

Scheme 3. Complex 3a heterolytically cleaves H₂ to generate Ir-hydride complex 4a. The activation of H₂ is proposed to take place initially at the Ir-O bond, generating complex 4a' that subsequently rearranges to 4a.
The reaction of complex 3a with H₂ in CD₂Cl₂ in the presence of NEt₃ (10 eq.) instantly leads to the formation of 4a. Interestingly, complex 4a completely disappears within 24 hours upon standing at room temperature and a new Ir-hydride species is obtained. This new Ir-hydride species displays a singlet in the ³¹P{¹H} NMR spectrum at 26.10 ppm in CD₂Cl₂. A hydride resonance is observed at -16.82 ppm (d, Jₚ-H = 31.1 Hz) by ¹H NMR spectroscopy, which is slightly more upfield compared to 4a (-13.73 ppm in CD₂Cl₂). Interestingly, the aromatic region integrates for 13 protons (instead of the expected 14) and a singlet at 7.75 ppm is observed. Analysis with HR-MS (FD⁺) showed a peak with an m/z of 725.21166, which corresponds to the loss of HCl from complex 4a. Based on these observations this new Ir-hydride complex is proposed to be complex 5a, which is the result of intramolecular C-H activation.¹⁰ It is proposed that complex 5a is generated via initial deprotonation and dehalogenation of 4a, generating 5a'. In this Ir-hydride complex the ligand is deprotonated and P,O-coordinated similar to 3a. Complex 5a' then heterolytically cleaves H₂ to form Ir-dihydride complex 5a''. Reductive elimination of H₂ from this species 5a'' would yield a coordinatively unsaturated and highly reactive Ir intermediate (5a''') that could undergo intramolecular C-H activation of the sulfonamide phenyl ring, resulting in complex 5a.

Scheme 4. Complex 2a reacts with NEt₃ and H₂ generating complex 4a, which over time forms complex 5a via intramolecular C-H activation. The formation of 5a is proposed to proceed via initial deprotonation and dehalogenation generating intermediate 5a', followed by the heterolytic cleavage of H₂, generating dihydride intermediate 5a''. From intermediate 5a'' H₂ is released via reductive elimination generating an Ir intermediate (5a''') that undergoes intramolecular C-H activation of the sulfonamide phenyl ring generating 5a.
Rhodium complex 3b showed similar reactivity toward H\textsubscript{2} as observed for 3a. Pressurizing a solution of 3b in THF with H\textsubscript{2} (5 bar) instantly led to the clean formation of Rh-hydride complex (4b), as was evident from the appearance of a hydride resonance at -11.41 ppm (doublet-of-doublet, \(J_{P-H} = 44.5\) Hz, \(J_{Rh-H} = 17.0\) Hz) in the \(^1\)H NMR spectrum.\[^\text{11}\] However, complex 4b was found to be unstable, even under inert atmosphere. Formation of a brown precipitate in the reaction mixture was observed after 2 hours, which is indicative for the formation of rhodium nanoparticles. The formed decomposition products could not be satisfactorily characterized.

6.2.3 Alkyne activation with 3a followed by intramolecular C-N bond formation.

The smooth and selective reactivity of complex 3a toward heterolytic H\textsubscript{2} activation and follow-up intramolecular C-H cleavage triggered our interest in the intermolecular bifunctional activation of acidic C-H bonds.\[^\text{12}\] Complex 3a proved stable in a THF solution containing an excess dimethyl malonate (10 eq.), even at elevated temperature (50 °C). In contrast, addition of phenylacetylene led to formation of two new species after 15 minutes at 50 °C. The \(^{31}\)P\{\(^1\)H\} NMR spectrum of this mixture initially displayed two singlets at 33.14 and 30.98 ppm in a ratio of 5:1, see Figure 3 bottom spectrum. However, this ratio gradually changed over time, converging to a single product (6a) (see Figure 3). Inspection of the \(^{13}\)C\{\(^1\)H\} NMR spectrum of this single species excluded the formation of the anticipated Ir-phenylacetylide complex, which would be formed via proton transfer from the terminal alkyne to the ligand, as the appropriate signals for such an Ir(≡CPh) fragment were not observed.\[^{12a, 12b}\] Rather unexpectedly, a doublet at 114.06 (d, \(J_{C-P} = 11.7\) Hz, CH) was detected.
Crystals suitable for X-ray diffraction were obtained via slow diffusion of pentane into a THF solution of complex 6a. The molecular structure establishes the formation of an Ir-vinyl complex containing an unusual four-membered Ir-P-N-C ring, see Figure 4. The Ir-P-N-C ring is essentially flat with bond angles of $\angle P_1$-Ir$_1$-C$_1$: 69.21(9)$^\circ$, $\angle$Ir$_1$-P$_1$-N$_1$: 88.48(9)$^\circ$, $\angle$P$_1$-N$_1$-C$_1$: 100.26(19)$^\circ$ and $\angle$N$_1$-C$_1$-Ir$_1$: 101.91(19)$^\circ$. Compared to complex 3a, the Ir-P and P-N bond lengths are slightly elongated (Ir$_1$-P$_1$ 2.2317(11) Å, P$_1$-N$_1$ 1.717(3) Å). The N$_1$-S$_1$ bond length of 1.653(3) Å clearly points to an N-S single bond, while the C$_1$-C$_2$ bond length of 1.338(5) Å indicates a C-C double bond. Based on these data complex 6a is best depicted as the Ir-vinyl complex, illustrated in Figure 4. To the best of our knowledge only three complexes containing a four-membered M-P-N-C ring have been reported in literature.\textsuperscript{[13]} Furthermore, this is the first example of reported with iridium as well as the first structure that is generated from an alkyne, making the vinyl fragment a unique exo-cyclic entity. Four-membered M-P-N-C rings wherein C is a carbene are more common in literature, particularly with ruthenium.\textsuperscript{[14]}

Figure 3. $^{31}$P$[^1]H$ NMR spectra of the reaction of complex 3a with phenylacetylene at 50 °C over the course of 120 minutes.
From the *in situ* $^{31}$P{$^1$H} NMR study illustrated in Figure 3, complex 6a appears to be preceded by another complex. This intermediate is proposed to be the corresponding Ir-acetylide species that was initially anticipated, see Scheme 5 complex 7a. In an attempt to characterize complex 7a, the reaction of phenylacetylene and complex 3a was monitored by $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy at 0 °C. The obtained $^{13}$C{$^1$H} NMR spectrum supported the intermediacy of species 7a in this reaction, as signals at 102.70 (d, J = 6.4 Hz, $C_{\text{quat}}$) and 94.86 (s, $C_{\text{quat}}$) indicate the $sp$ carbons of the acetylide fragment.$^{[12b]}$

Scheme 5. Complex 3a reacts with phenylacetylene to generate Ir-alkyl complex 7a, which rearranges to Ir-vinyl complex 6a within 3 hours at 50 °C.
Complex 6a is proposed to form via initial proton transfer from the phenylacetylene to the METAMORPhos backbone (generating 7a), followed by a formal intramolecular anti-Markovnikov hydroamination onto the resulting acetylide species. This C-N bond formation would involve nucleophilic attack of the nitrogen onto the α-carbon of the Ir(C≡CPh) fragment. To support this proposed mechanism, DFT calculations were performed (BP86, def2-TZVP) and the obtained energy profile is displayed in Figure 5. The combination of complex 3a + phenylacetylene was used as reference point (0.0 kcal mol\(^{-1}\)). Formation of Ir-acetylide complex 7a is slightly downhill by 1.5 kcal mol\(^{-1}\). From here the most energetically favored pathway to 6a proceeds via proton transfer from the N-H of the ligand* to the β-carbon of the acetylide through TS1, which is endergonic by 17.6 kcal mol\(^{-1}\). This generates a cationic high-oxidation state \(\text{Ir}^{V}\)-vinylidene intermediate (Int, 13.7 kcal mol\(^{-1}\)), wherein the ligand is anionically charged but monodentate P-coordinated.** Nucleophilic attack of the nitrogen of the ligand onto the α-carbon of the vinylidene via TS2 (endergonic by 18.3 kcal mol\(^{-1}\)) generates complex 6a. This product is found to be exergonic by 6.7 kcal mol\(^{-1}\) relative to the starting materials. An alternative concerted mechanism involving direct N-H syn-addition over the \(\text{C≡C}\) bond could not be found by DFT calculations. The pathway involving protonation via a sulfon O-H was found to be slightly higher in energy (initial proton transfer step was endergonic by 18.6 kcal mol\(^{-1}\), see experimental section) relative to the described route.

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* Protonolysis of a Pd-alkyl species by the N-H of a METAMORPhos ligand was previously suggested to occur in the generation of a \(\text{Pd}^{I}\)_2 species, see Chapter 5.

** Vinylidenes are generally formed via an \(\eta^2\)-alkyne to \(\eta^1\)-vinylidene rearrangement involving a 1,2-proton shift.\(^{[15]}\) This pathway is unlikely here, as it would necessitate decoordination of the anionic METAMORPhos. Initial formation of complex 7a was also confirmed experimentally by NMR spectroscopy.
Figure 5. Potential energy diagram (DFT, BP86, def2-TZVP) for the formation of 6a from 7a; $\Delta G^\circ_{298K}$ is in kcal mol$^{-1}$, with complex 3a + phenylacetylene taken as reference point.

6.3 Conclusions

The coordination of METAMORPhos ligand 1 with [Cp*MCl$_2$]$_2$ (M = Ir or Rh) and the potential role of the ligand in bifunctional substrate activation is investigated. Complexes 3a (Ir) and 3b (Rh), wherein the ligand is deprotonated, were found to be active in the bifunctional activation of H$_2$, generating monohydride complexes 4a-b. Complex 4a is susceptible to further reaction with H$_2$ in the presence of NEt$_3$, leading to complex 5a which is formed via intramolecular C-H activation of the sulfonamide phenyl ring. The formation of 5a likely proceeds via the formation of Ir-dihydride species 5a'', which releases H$_2$ to create a highly active Ir$^1$ intermediate (5''') prior to C-H oxidative addition. Complex 3a is also active in the bifunctional intermolecular activation of phenylacetylene, which initially results in Ir-acetylide complex 7a. This complex selectively rearranges within hours to the unusual Ir-P-N-C ring complex 6a. DFT calculations suggest that formation of this species proceeds via proton transfer from the ligand to the β-carbon of 7a, generating an Ir$^V$-vinylidene intermediate (Int). Subsequent nucleophilic attack of the nitrogen onto the electrophilic α-carbon results in formation of 6a, bearing a unique exo-cyclic vinyl unit.

These examples illustrate the bifunctional potential of METAMORPhos in these type of complexes. For instance, complexes with METAMORPhos ligands lacking aromatic C-H bonds would be interesting to investigate for intermolecular C-H bond activation, as subsequent release of H$_2$ (via protonation of the Ir-H bond with the N-H of the ligand), could generate a complex with the capabilities of activating a second substrate. Such an approach could generate catalytic systems for selective aromatic H/D exchange or C-C bond formation.
6.4 Experimental section

General procedures
All reactions were carried out in dry glassware under nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. THF, toluene and pentane were distilled from sodium under dinitrogen, \( \text{CH}_2\text{Cl}_2 \) was collected from an MB SPS-800. Deuterated solvents were degassed by four freeze-pump-thaw cycles and dried over molecular sieves (4Å). NMR spectra were measured on a Bruker AMX 400 (\( ^1\text{H}: 400.1 \text{ MHz} \), \( ^{13}\text{C}: 100.6 \text{ MHz} \) and \( ^{31}\text{P}: 162.0 \text{ MHz} \)) or on a Varian Mercury 300 (\( ^1\text{H}: 300.1 \text{ MHz} \)) spectrometer. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. High resolution mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV mass spectrometer.

Materials
All reagents were purchased from commercial suppliers and used without further purification: Chlorodiphenylphosphine (Sigma Aldrich), trichlorophosphine (Sigma Aldrich), 4-butylbenzene-1-sulfonamide (ABCR GmbH), \([\text{Cp}^*\text{IrCl}_2]^2\) (Strem chemicals) and \([\text{Cp}^*\text{RhCl}_2]^2\) (Strem chemicals). Triethylamine (Sigma Aldrich) was freshly distilled and stored over molecular sieves (4 Å), Ligand 1 was prepared according to a literature procedure.\(^{15a}\)

Computational details:
Geometry optimizations were carried out with the Turbomole program package, coupled to the PQS Baker optimizer via the BOpt package, at the spin unrestricted ri-DFT level using the BP86 functional, the resolution-of-identity (ri) method, and the def2-TZVP basis set for the geometry optimizations.\(^{16}\)

Complex 2a
Ligand 1 (190.6 mg) was dissolved in \( \text{CH}_2\text{Cl}_2 \) (2.0 mL) and \([\text{Cp}^*\text{IrCl}_2]^2\) (191.0 mg, 0.5 equivalent) was added. The formed suspension was stirred for 1 hour and a clear deep orange solution was obtained. The reaction mixture was concentrated to approximately 0.5 mL and pentane was added until an orange precipitate was formed. The suspension was carefully concentrated under high vacuum and 2a was obtained quantitatively. \(^{31}\text{P}(\text{H})\) NMR (162 MHz, \( \text{CD}_2\text{Cl}_2 \), ppm): \( \delta 37.57 \) (s); \(^1\text{H} \) NMR (400 MHz, \( \text{CD}_2\text{Cl}_2 \), ppm): \( \delta 7.87 \) (dt, \( J = 12.4, 7.4 \text{ Hz} \), 4H), 7.48-7.43 (m, 2H), 7.39 (m, 5H), 7.16 (d, \( J = 8.3 \text{ Hz} \), 2H), 6.94 (d, \( J = 8.3 \text{ Hz} \), 2H), 2.54 (t, \( J = 7.6 \text{ Hz} \), 2H), 1.57-1.48 (m, 2H), 1.31 (d, \( J = 2.4 \text{ Hz} \), 15H), 1.30 (m, 2H), 0.94 (t, \( J = 7.8 \text{ Hz} \), 3H); \(^1\text{H}(-\text{P})\) NMR (400 MHz, \( \text{CD}_2\text{Cl}_2 \), ppm): \( \delta 7.87 \) (d, \( J = 7.4 \text{ Hz} \), 4H), 7.48-7.43 (m, 2H), 7.39 (m,
probably due to trace amount of HCl in solution, which regenerates

toc, 5H), 7.16 (d, J = 8.3 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 2.54 (t, J = 7.6 Hz, 2H), 1.57-1.48 (m, 2H), 1.31 (s, 15H), 1.30 (m, 2H), 0.94 (t, J = 7.8 Hz, 3H); $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 147.71 (s, C$_{quat}$), 138.94 (s, C$_{quat}$), 134.10 (d, J = 11.8 Hz, CH), 132.00 (d, J = 2.2 Hz, CH), 128.38 (s, CH), 128.70 – 128.06 (d, J = 63.0 Hz C$_{quat}$), 127.90 (d, J = 11.4 Hz, CH), 126.35 (s, CH), 93.33 (d, J = 3.5 Hz, C$_{quat}$), 35.48 (s, CH$_2$), 33.41 (s, CH$_2$), 22.39 (s, CH$_2$), 13.89 (s, CH$_3$), 8.19 (s, CH$_3$); HR-MS (FAB$^+$): m/z calcd. for C$_{32}$H$_{39}$Cl$_2$IrNO$_2$PS [M]$^+$: 795.1432, observed: 795.1443.

Complex 2b
Ligand 1 (165.0 mg) was dissolved in CH$_2$Cl$_2$ (2.0 mL) and [Cp*RhCl$_2$]$_2$ (128.0 mg, 0.5 equivalent) was added. The formed suspension was stirred for 1 hour and a deep red solution was obtained. The reaction mixture was concentrated to approximately 0.5 mL and pentane was added until a red precipitate was formed. The suspension was carefully concentrated under high vacuum and 2b was obtained quantitatively. $^{31}$P$^1$(H) NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 67.58 (d, J$_{p-Rh} = 151.7$ Hz); $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.92 (dd, J = 11.5, 7.2 Hz, 4H), 7.52 – 7.44 (m, 2H), 7.41 – 7.35 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 11.6 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 2.55 (t, J = 7.5 Hz, 2H), 1.53 (m, 2H), 1.34 (m, 2H), 1.30 (d, J = 3.9 Hz, 15H), 0.92 (t, J = 8.0 Hz 3H); $^1$H$^{31}$P) NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.92 (d, J = 7.2 Hz, 4H), 7.52 – 7.44 (m, 2H), 7.41 – 7.35 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 7.10 (s, 1H), 6.92 (d, J = 8.4 Hz, 2H), 2.55 (t, J = 7.5 Hz, 2H), 1.53 (m, 2H), 1.34 (m, 2H), 1.30 (s, 15H), 0.92 (t, J = 8.0 Hz 3H); $^{13}$C$^1$(H) NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 147.72 (s, C$_{quat}$), 138.80 (s, C$_{quat}$), 134.14 (d, J = 11.9 Hz, CH), 132.11 (d, J = 2.3 Hz, CH), 128.49 (d, J = 51.2 Hz, C$_{quat}$), 128.35 (s, CH), 128.17 (d, J = 11.0 Hz, CH), 126.32 (s, CH), 99.80 (dd, J = 6.9, 3.4 Hz, C$_{quat}$), 35.48 (s, CH$_2$), 33.40 (s, CH$_2$), 22.39 (s, CH$_2$), 13.88 (s, CH$_3$), 8.69 (s, CH$_3$); HR-MS (FAB$^+$): m/z calcd. for C$_{32}$H$_{39}$Cl$_2$IrNO$_2$P$_1$Rh$_1$S$_1$ [M]$^+$: 705.0872, observed: 705.08498.

Complex 3a
To a solution of 2a (350 mg) in CH$_2$Cl$_2$ (3 mL) was added sodium acetate (10-15 equivalents) and the suspension was stirred for 24 hours at room temperature. A slight color change from deep orange to orange was observed. The reaction mixture was filtered and concentrated to approximately 0.5 mL and pentane (5 mL) was added under vigorous stirring. The formed precipitate was filtered, washed with pentane (3 × 5 mL) and collected as yellow/orange solid (287 mg, yield 86%).

Note: Care should be taken in using CHCl$_3$ as solvent, because reprotonation of 3a occurs, probably due to trace amount of HCl in solution, which regenerates 2a.

$^{31}$P$^1$(H) NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 48.80 (s), (δ 45.71 in THF-d$_8$); $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.86 (d, J = 8.3 Hz, 2H), 7.74 – 7.60 (br. m, 2H), 7.60 – 7.38 (br. m, 8H), 7.21
(d, J = 7.9 Hz, 2H), 2.65 (t, J = 7.7 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.51 (d, J = 2.1 Hz, 15H), 1.40 – 1.29 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); $^1$H$^{31}$P NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.86 (d, J = 8.3 Hz, 2H), 7.68 (br. s, 2H), 7.58 – 7.40 (m, 8H), 7.21 (d, J = 7.9 Hz, 2H), 2.65 (t, J = 7.7 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.51 (s, 15H), 1.40 – 1.29 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); $^{13}$C$^1$H NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 147.18 (s, C$_{quat}$), 138.8 (d, 60Hz, C$_{quat}$), 137.86 (s, C$_{quat}$), 133.24 (s, C$_{quat}$), 132.41 (d, J = 11.4 Hz, CH), 132.11 (d, J = 11.2 Hz, CH), 130.68 (d, J = 25.7 Hz, CH), 128.55 (s, CH), 128.40 – 127.92 (m, CHs), 91.80 (d, J = 2.8 Hz, C$_{quat}$), 35.68 (s, CH$_2$), 33.66 (s, CH$_2$), 22.58 (s, CH$_2$), 13.99 (s, CH$_3$), 9.02 (s, CH$_3$); HR-MS (FAB$^+$): m/z calcd. for C$_{32}$H$_{38}$ClIrNO$_2$PS [M+H]$^+$: 760.1749, observed: 760.1751 Anal. Calcd. for C$_{32}$H$_{38}$ClIrNO$_2$PS: C, 50.61; H, 5.04; N, 1.84, found: C, 50.73; H, 4.99, N, 1.89.

**Complex 3b**

To a solution of 2b (150 mg) in CH$_2$Cl$_2$ (2 mL) was added sodium acetate (10-15 equivalents) and the deep red suspension was stirred for 24 hours at room temperature. The reaction mixture was filtered and concentrated to approximately 0.5 mL and pentane (5 mL) was added under vigorous stirring. The formed precipitate was filtered, washed with pentane (3 × 5 mL) and collected as red solid (120 mg, yield 84 %). $^{31}$P$^1$H NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 68.39 (d, J = 129.5 Hz); $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.82 (d, J = 8.3 Hz, 2H), 7.68 – 7.59 (br. m, 4H), 7.46 (br. m, 6H), 7.18 (d, J = 8.0 Hz, 2H); 2.63 (t, J = 7.7 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.47 (d, J = 3.3 Hz, 15H), 1.41 – 1.29 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); $^1$H$^{31}$P NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.82 (d, J = 8.3 Hz, 2H), 7.68 – 7.59 (br. m, 4H), 7.46 (br. m, 6H), 7.18 (d, J = 8.0 Hz, 2H); 2.63 (t, J = 7.7 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.47 (s, 15H), 1.41 – 1.29 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H), $^{13}$C$^1$H NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 146.72 (s, C$_{quat}$), 140.37 (s, C$_{quat}$), 138.52 (d, J = 56.5 Hz, C$_{quat}$), 134.13 (d, J = 68.1 Hz, C$_{quat}$), 132.26 (d, J = 11.5 Hz, CH), 131.99 (d, J = 10.9 Hz, CH), 130.55 (d, J = 21.8 Hz, CH), 128.47 (br. s, CH), 128.03 (d, J = 10.8 Hz, CH), 127.63 (br. s, CH), 98.74 (dd, J = 7.5, 2.8 Hz, C$_{quat}$), 35.63 (s, CH$_2$), 33.58 (s, CH$_2$), 22.52 (s, CH$_2$), 13.96 (s, CH$_3$), 9.25 (s, CH$_3$); HR-MS (FD$^+$): m/z calcd. for C$_{32}$H$_{38}$ClIrNO$_2$PS [M+H]$^+$: 669.11044, observed: 669.11711; Anal. Calcd. for C$_{32}$H$_{38}$ClIrNO$_2$PS: C, 57.36; H, 5.72; N, 2.09 found: C, 57.22; H, 5.79, N, 2.04.

**Complex 4a**

A solution of 3a (25 mg) in THF-$d_8$ (0.7 mL) was pressurized in a J-Young NMR tube with H$_2$ (5 bar) after rigorous purging. After 30 minutes the quantitative formation of 4a was observed by NMR spectroscopy. $^{31}$P$^1$H NMR (162 MHz, THF-$d_8$, ppm): δ 40.98 (s), (δ 45.18 in CD$_2$Cl$_2$) δ; $^1$H NMR (400 MHz, THF-$d_8$, ppm): δ 7.86 – 7.73 (m, 5H), 7.42 – 7.31 (m, 6H), 7.10 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 2.53 (t, J = 7.8 Hz, 2H), 1.58-1.50 (m, 2H), 1.52 (d, J = 1.5 Hz, 15H), 1.36-1.28 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H), -1.43 (d, J = 39.1 Hz, 1H), $^1$H$^{31}$P NMR (400 MHz, THF-$d_8$, ppm): δ 7.84 – 7.79 (m, 3H), 7.76 (dd, J = 7.6, 1.8 Hz, 2H), 7.39 – 7.33 (m,
Complex 4b

A solution of 3b (25 mg) in THF-\(d_8\) (0.7 mL) was pressurized in a J-Young NMR tube with \(H_2\) (5 bar) after rigorous purging. After 30 minutes the quantitative formation of 4b was observed by NMR spectroscopy. Complex 4b was found to be unstable, even under \(H_2\) atmosphere, with approximately 50% decomposition observed in after 16 hours at room temperature.

Complex 5a

To a solution of 2a (100 mg, 0.126 mmol) in \(CH_2Cl_2\) (5 mL) was added NEt\(_3\) (175 µL, 1.26 mmol). The reaction mixture was flushed with \(H_2\) (balloon) for 30 minutes, resulting in a color change from orange to yellow/orange and then stirred at room temperature for 24 hours. The reaction mixture was concentrated and washed with pentane (3 x 3 mL) and 5a was obtained as yellow powder (yield 85%). \(^{31}P\(\{^1H\}\) NMR (162 MHz, \(CD_2Cl_2\), ppm): \(\delta\) 26.10 (s); \(^1H\) NMR (400 MHz, \(CD_2Cl_2\), ppm): \(\delta\) 7.75 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.59 (dd, J = 11.0, 7.5 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.40 (t, J = 6.6 Hz, 2H), 7.29 (t, J = 6.8 Hz, 1H), 7.14 (s, 3H), 6.61 (d, J = 7.8 Hz, 1H), 2.58 – 2.49 (m, 2H), 1.68 – 1.54 (m, 2H), 1.51 (d, J = 1.2 Hz, 15H), 1.41 – 1.28 (m, 2H), 0.94 (t, J = 9.4, 3H), -16.87 (d, J = 31.1 Hz, 1H), \(^{31}P\(\{^{13}C\}\) NMR (400 MHz, \(CD_2Cl_2\), ppm): \(\delta\) 7.75 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.5 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.40 (t, J = 6.6 Hz, 2H), 7.29 (t, J = 6.8 Hz, 1H), 7.14 (s, 3H), 6.61 (d, J = 7.8 Hz, 1H), 2.58 – 2.49 (m, 2H), 1.68 – 1.54 (m, 2H), 1.51 (s, 15H), 1.41 – 1.28 (m, 2H), 0.94 (t, J = 9.4, 3H), -16.87 (s, 1H), \(^{13}C\(\{^1H\}\) NMR (101 MHz, \(CD_2Cl_2\), ppm): \(\delta\) 148.82 (s, \(C_{quat}\)), 147.55 (s, \(CH\)), 145.59 (d, J = 69.1 Hz, \(C_{quat}\)), 141.85 (s, \(C_{quat}\)), 140.24 (d, J = 53.2 Hz, \(C_{quat}\)), 133.55 (d, J = 11.6 Hz, \(C_{quat}\)), 132.67 (d, J = 10.7 Hz, \(CH\)), 131.93 (d, J = 11.5 Hz, \(CH\)), 129.15 (s, \(CH\)), 128.69 (s, \(CH\)), 127.41 (d, J = 10.5 Hz, \(CH\)), 121.95 (s, \(CH\)), 120.68 (s, \(CH\)), 94.87 (br. s, \(C_{quat}\)), 35.45 (s, \(CH_2\)), 34.23 (s, \(CH_2\)), 22.83 (s, \(CH_2\)), 14.22 (s, \(CH_3\)), 9.63 (s, \(CH_3\)); \textbf{HR-MS} (FD\(^+\)): \(m/z\) calcd. for \(C_{32}H_{39}IrNO_2PS\ [M]^{+}\: 725.20683,\) observed: 725.21166.
Complex 6a
Complex 3a (50 mg, 0.066 mmol) was dissolved in THF (2 mL) and phenylacetylene was added (7.2 µL, 0.066 mmol) and the reaction mixture was stirred at 50 °C for 3 hours. The reaction mixture was allowed to cool to room temperature and thereafter concentrated under vacuum. To the obtained yellow solid was added 0.2 mL CH$_2$Cl$_2$ followed by 5 mL pentane under stirring. The formed suspension was stirred for 15 minutes and then filtered. The yellow residue was washed with pentane (2 × 3 mL) and dried under vacuum. Complex 6a was obtained as yellow solid (yield 76%).

$^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 30.98 (s);

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 8.45 – 8.33 (m, 2H), 7.62 – 7.53 (m, 2H), 7.54 – 7.47 (m, 6H), 7.47 – 7.40 (m, 4H), 7.10 – 7.01 (m, 4H), 6.94 (t, $J$ = 7.3 Hz, 1H), 6.88 (d, $J$ = 4.4 Hz, 1H), 2.50 (t, $J$ = 7.6 Hz, 2H), 1.53 – 1.50 (m, 2H), 1.28 (d, $J$ = 2.6 Hz, 15H), 1.28 – 1.17 (m, 2H), 0.84 (t, $J$ = 7.3 Hz, 3H);

$^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 149.28 (s, C$_{quat}$), 143.23 (s, C$_{quat}$), 139.83 (d, $J$ = 14.7 Hz, CH), 139.09 (s, C$_{quat}$), 134.42 (d, $J$ = 63.5 Hz, C$_{quat}$), 134.13 (d, $J$ = 2.6 Hz, CH), 133.45 (d, $J$ = 11.5 Hz, CH), 132.83 (d, $J$ = 48.3 Hz, C$_{quat}$), 125.53 (s, CH), 114.06 (d, $J$ = 11.7 Hz, CH), 95.46 (d, $J$ = 3.5 Hz, C$_{quat}$), 36.13 (s, CH$_2$), 33.60 (s, CH$_2$), 23.01 (s, CH$_2$), 14.01 (s, CH$_3$), 8.55 (s, CH$_3$);

HR-MS (FD$^+$): m/z calcd. for C$_{40}$H$_{44}$ClIrNO$_2$P$_1$S$_1$ [M$^+$]: 859.21248 observed: 859.21648.

Complex 7a
Complex 3a (25 mg, 0.033 mmol) was dissolved in THF-d$_8$ (0.7 mL) and phenylacetylene was added (3.6 µL, 0.033 mmol) at 0 °C. All NMR spectra were obtained at 0 °C after 3 hours of reaction. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 33.14 (s);

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 8.04 – 7.96 (m, 2H), 7.93 (dd, $J$ = 11.8, 7.8 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.45 – 7.36 (m, 5H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.22 – 7.10 (m, 3H), 7.09 – 7.02 (m, 2H), 6.82 (t, $J$ = 7.1 Hz, 2H), 2.48 (t, $J$ = 7.7 Hz, 2H), 1.66 – 1.50 (m, 2H), 1.47 (d, $J$ = 1.8 Hz, 15H), 1.33 – 1.22 (m, 2H), 0.92 (t, $J$ = 7.3 Hz, 3H);

$^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 147.31 (s, C$_{quat}$), 142.37 (s, C$_{quat}$), 138.94 (s, CH), 135.76 (d, $J$ = 15.0 Hz, CH), 133.91 (s, CH), 132.83 (d, $J$ = 2.6 Hz, CH), 132.72 – 132.53 (m), 132.29 (s, CH), 131.55 (s, CH), 128.62 (s), 128.39 – 127.82 (m), 127.04 (s), 125.25 (s), 124.87 – 124.76 (m), 124.70 (s, C$_{quat}$), 102.70 (d, $J$ = 6.4 Hz, C$_{quat}$), 95.74 (d, $J$ = 3.4 Hz, C$_{quat}$), 94.86 (s, C$_{quat}$), 35.87 (s, CH$_2$), 33.98 (s, CH$_2$), 22.93 (s, CH$_2$), 14.05 (s, CH$_3$), 8.26 (s, CH$_3$).
Figure 6. Potential energy diagram (DFT, BP86, def2-TZVP) for the formation of Int from 7a via protonation with the sulfon group; $\Delta G^\circ_{298K}$ is in kcal mol$^{-1}$ complex 3a + phenylacetylene are used as reference point.
6.4 References


