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Intermolecular C–H activation with an Ir-METAMORPhos piano-stool complex – multiple reaction steps at a reactive ligand†

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Substrate activation by means of a reactive ligand is a topic of much interest. Herein we describe a stoichiometric anti-Markovnikov C–N bond formation involving ligand reactivity in multiple steps along the reaction coordinate, including ligand assisted substrate (de)protonation and C–N bond formation, as illustrated by a combined experimental, spectroscopic and computational study. This affords a highly unusual four-membered iridacycle bearing an exo-cyclic C=C double bond.

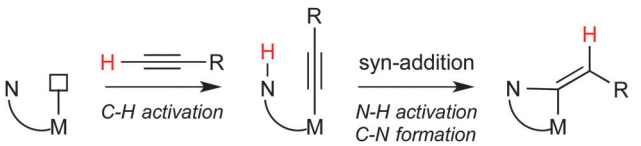

Fig. 1 Sequential C–H and N–H bond activation with subsequent C–N bond formation on a reactive ligand scaffold.

Metal–ligand bifunctional substrate activation has recently evolved as a valuable strategy in homogeneous catalysis. Hydrogen-bond interactions and acid–base reactivity are often-encountered strategies in this context.[1,2] Prime examples of reactive ligands with internal Brønsted-active sites that can undergo reversible deprotonation are those containing primary or secondary amines. The nitrogen atom may be in the coordination sphere of the transition metal or located in the ligand backbone, having no direct interaction with the metal.[3] C–H activation remains to be a topic of intense research, with a major focus on site-specific and regioselective functionalization. Intramolecular ligand-assisted metal-mediated C–H activation, *via* a directing group, is frequently utilized[4] but intermolecular C–H activation facilitated by a reactive ligand (Fig. 1) that functions as internal base is much less explored.[5]

However, elegant work by Grotjahn using imidazolylphosphines as reactive ligands to enhance alkyne C–H activation has demonstrated the feasibility of this approach for the hydration of alkynes.[6] The related hydroaddition of amines to unsaturated hydrocarbons is an attractive and atom-efficient protocol to form C–N bonds. Hydroamination with late transition metal complexes typically proceeds *via* initial coordination and activation of the hydrocarbon, with follow-up (external) nucleophilic attack of the (activated) amine and proton transfer.[7] Examples where C–H activation of an unsaturated hydrocarbon precedes the overall *syn*-addition of an amine are rare[8] and no structurally characterized complex has been reported, to the best of our knowledge. We hypothesized that metal–ligand bifunctional activation of a hydrocarbon could allow for direct observation of this unusual pathway, which could potentially open up new avenues for hydroaddition chemistry and catalysis. Ligands that combine more than one type of reactivity in the scaffold are uncommon[9] but these designs could provide entry into site-selective activation and functionalization of substrates.

Sulfonamidophosphine ligands (coined METAMORPhos), which are accessible from commercially available sulfonamides and chlorophosphine precursors, have been demonstrated to combine proton responsive character at nitrogen with hydrogen bonding properties upon coordination to transition metals.[10] Intermolecular C–H activation mediated by this ligand scaffold has not been observed to date. METAMORPhos contains two potentially reactive ligand sites, namely the sulfonyl oxygen and the nitrogen, of which the former can coordinate to metal ions (both as neutral or anionic donor), while the latter is part of the second coordination sphere. Iridium piano-stool complexes have been used regularly for a number of bond activation processes, including the use of noninnocent ligands in the coordination sphere of Ir.[11] Herein, we demonstrate the key steps of METAMORPhos-assisted C–H activation of alkynes in the coordination sphere of Ir^{III} and subsequent overall *syn*-addition of the H–N(R) ligand fragment over the C≡C bond. The end-product contains a unique four-membered metallacycle with an exo-cyclic double bond, as

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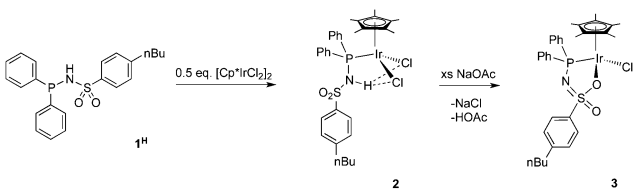
confirmed by X-ray crystal structure determination and NMR spectroscopy.‡ DFT calculations provide insight in the pathway for this unusual transformation.

Mixing two molar equivalents of ligand $\mathbf{1^H}$ with Ir-precursor $[IrCl(Cp^*)(\mu\text{-}Cl)]_2$ in CD_2Cl_2 instantly led to complete consumption of starting materials and formation of a single species, which was characterized by multinuclear NMR spectroscopy and HR-MS spectrometry as neutral P-coordinated complex **2** (see Scheme 1). An X-ray crystal structure determination supports this conformation in the solid state (Fig. 2, left). Hydrogen bond interactions between the N–H of the METAMORPhos ligand and the chloride ligands Cl_1 and Cl_2 were observed [$N_1\cdots Cl_1$ 3.1451(13), $N_1\cdots Cl_2$ 3.2529(14)] (see Table S1 in the ESI†).[12]

Addition of **2** to a suspension of sodium acetate (NaOAc) in CH_2Cl_2 at room temperature led to complete conversion of this complex to a new species **3** (as could easily by observed by ^{31}P NMR spectroscopy), formulated as $IrCl(Cp^*)(\kappa^2\text{-P,O-}\mathbf{1})$ (see Scheme 1), based on multinuclear NMR spectroscopy and HR-MS spectrometry and supported by single crystal X-ray structure determination (Fig. 2, right). Compared to the bond lengths found in the precursor species **2**, the N_1–S_1 bond is shortened (1.5464(13) Å) while the S–O_1 bond (1.5098(11) Å) is elongated for **3**, which clearly confirms that the ligand has indeed undergone deprotonation.



Scheme 1 Preparation of neutral monodentate P-coordinated complex **2** from $\mathbf{1^H}$ with $[IrCl(Cp^*)(\mu\text{-}Cl)]_2$ and subsequent deprotonation to give P,O-coordinated complex **3**.

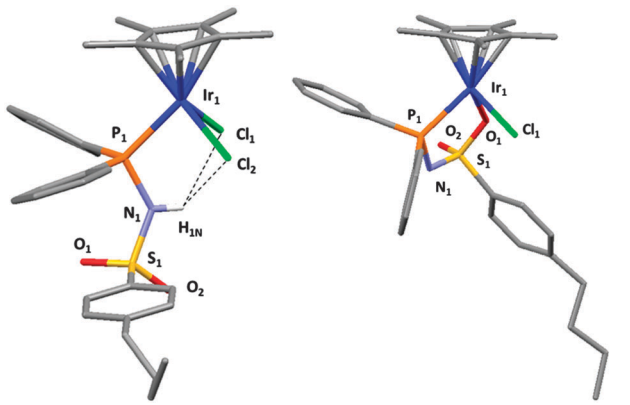
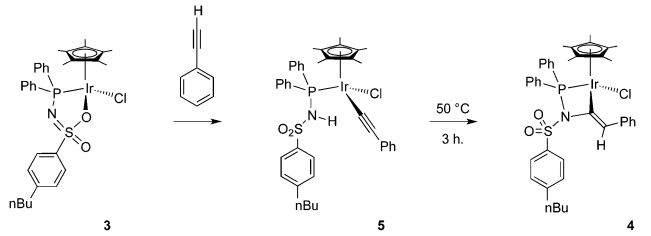


Fig. 2 Left: X-ray crystal structure of **2**. Right: X-ray crystal structure of **3**. Selected bond lengths (Å) and angles (°), for **2**: Ir_1–P_1 2.2838(4); Ir_1–Cl_1 2.3956(4); Ir_1–Cl_2 2.4061(4); P_1–N_1 1.7019(13); N_1–S_1 1.6325(13); S_1–O_1 1.4351(12); S_1–O_2 1.4358(13); N_1–Cl_1 3.1451(13); N_1–Cl_2 3.2529(14); N_1–H_{1N}–Cl_1 119.8(19); N_1–H_{1N}–Cl_2 115.9(19). For **3**: Ir_1–P_1 2.2968(4); Ir_1–O_1 2.1630(10); Ir_1–Cl_1 2.3981(4); P_1–N_1 1.6535(13); N_1–S_1 1.5464(13); S_1–O_1 1.5098(11); S_1–O_2 1.4448(11); P_1–Ir_1–O_1 80.41(3).



Scheme 2 Complex **3** reacts with phenylacetylene to generate Ir-acetylide complex **5**, which rearranges to Ir-vinyl complex **4** within 3 hours at 50 °C.

With pre-activated species **3** in hand, we decided to investigate the ligand assisted intermolecular activation of alkynes, generating an Ir-phenylacetylide species *via* proton transfer from the terminal alkyne to the proton responsive ligand, which might allow for alternative reaction pathways in the context of selective hydrofunctionalization.[13] Addition of phenylacetylene to **3** led to the formation of a new species (^{31}P NMR: δ 31.0 ppm) after two hours at 50 °C. The $^{13}C\{^1H\}$ NMR spectrum showed no formation of the anticipated $Ir^{III}(C{\equiv}CPh)$ complex **5** (Scheme 2), but did reveal an unexpected doublet at 114.06 ppm (J_{C-P} = 11.7 Hz, *C*H), while the corresponding ^1H NMR spectrum showed a singlet at 6.88 ppm. The identity of the complex obtained could be determined *via* single crystal X-ray structure determination, obtained *via* slow diffusion of pentane into a THF solution of complex **4**. The resulting X-ray structure establishes the formation of an Ir-vinyl complex containing an unusual four-membered Ir–P–N–C ring, see Fig. 3.

The Ir–P–N–C ring is essentially flat, with a torsion angle $\angle Ir_1$–P_1–N_1–C_1 of −3.13°. The geometry of the metallacycle is very asymmetric, with bond angles of $\angle P_1$–Ir_1–C_1: 69.21(9)°, $\angle Ir_1$–P_1–N_1: 88.48(9)°, $\angle P_1$–N_1–C_1: 100.26(19)° and $\angle N_1$–C_1–Ir_1: 101.91(19)°. Compared to complex **3**, the P–N bond lengths are slightly elongated (P_1–N_1 1.6535(13), P_1–N_1 1.717(3) Å for **3** and **4** respectively). The N_1–S_1 bond length of 1.653(3) Å clearly points toward an N–S single bond, while the C_1–C_2 bond length of 1.338(5) Å indicates a C–C double bond. To the best of our

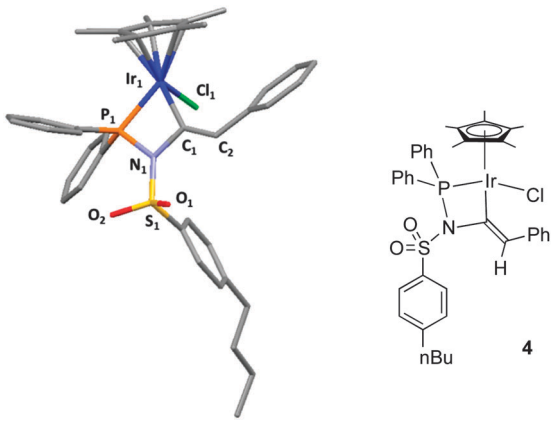


Fig. 3 X-ray structure and schematic representation of **4**. Selected bond lengths (Å) and angles (°): Ir_1–P_1 2.2317(11); Ir_1–C_1 2.077(3); Ir_1–Cl_1 2.4083(8); P_1–N_1 1.717(3); N_1–C_1 1.468(4); N_1–S_1 1.653(3); S_1–O_1 1.436(2); S_1–O_2 1.430(3); C_1–C_2 1.338(5); P_1–Ir_1–C_1 69.21(9); Ir_1–P_1–N_1 88.48(9); P_1–N_1–C_1 100.26(19); N_1–C_1–Ir_1 101.91(19).

knowledge only three complexes containing a four-membered M–P–N–C ring with an sp^2 hybridized carbon atom have been reported in literature.[14] This is the first example 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 divalent carbene are more common in literature, particularly with ruthenium.[15] Alkyne activation likely proceeds by concerted metalation–deprotonation after initial coordination of the π-system to Ir^{III}, facilitated by Cl^- dissociation in THF.[10] Proton-transfer to the more basic sulfonamide nitrogen is favored over protonation of the S=O, but temporary formation of –OH as a kinetic intermediate can not be excluded.[16]

Monitoring the unique conversion from **3** to this novel complex **4** by $^{31}P\{^1H\}$ NMR spectroscopy directly after addition of phenylacetylene at room temperature revealed the intermediacy of another species (^{31}P NMR: δ 33.1 ppm). In an attempt to characterize this complex, the reaction of phenylacetylene and complex **3** was monitored by ^1H, ^{31}P and ^{13}C NMR spectroscopy at 0 °C. Signals at 102.70 (d, J = 6.4 Hz, C_{quat}) and 94.86 (s, C_{quat}), in the $^{13}C\{^1H\}$ NMR spectrum support the involvement of the initially anticipated Ir^{III}(C≡CPh) species **5** in this reaction (Scheme 2).[5,6,8]

Complex **4** is proposed to form *via* initial proton transfer from the phenylacetylene to the METAMORPhos backbone (generating **5**), followed by a formal intramolecular anti-Markovnikov hydroamination onto the resulting acetylide species. This selective C–N bond formation, which occurs in an overall *syn* addition, would involve nucleophilic attack of the nitrogen onto the electrophilic α-carbon of the Ir(C≡CPh) fragment.[17] To support this proposed mechanism, DFT calculations were performed (BP86, def2-TZVP); the energetically most favored obtained energy profile is displayed in Fig. 4 (see ESI† for comparison with experimental metric parameters). The combination of (**3** + HCCPh) was used as reference point (0.0 kcal mol^{-1}). Formation of Ir-acetylide complex **5** is slightly downhill by 1.5 kcal mol^{-1}. From this observable intermediate, the most energetically favored pathway to **4** proceeds *via* initial 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

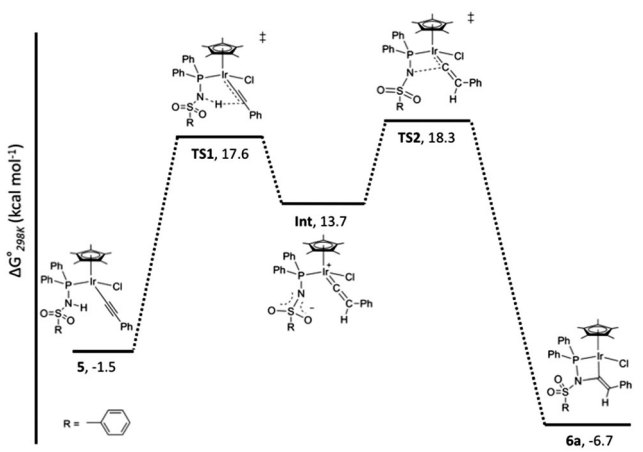


Fig. 4 Potential energy diagram (DFT, BP86, def2-TZVP) for the formation of **4** from **5**: ΔG°_{298K} is in kcal mol^{-1}, with (**3** + HCCPh) taken as reference point.

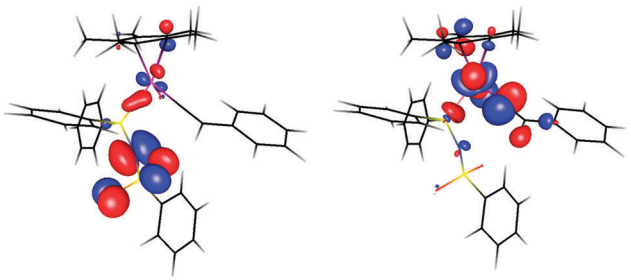


Fig. 5 HOMO (left) and LUMO (right) for complex **Int**.

intermediate **Int** (13.7 kcal mol^{-1}), wherein the anionic ligand is only monodentate P-coordinated.[18] The calculated HOMO and LUMO of this intermediate species support formulation as an electrophilic iridium(III)-vinylidene (Fig. 5). Subsequent 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 **4**, bearing a unique exo-cyclic vinyl unit. This product is exergonic by 6.7 kcal mol^{-1} relative to the starting materials. We were unable to find a transition state for the alternative concerted mechanism involving direct N–H *syn*-addition over the C≡C bond. The pathway involving protonation *via* a sulfone O–H was found to be slightly higher in energy (initial proton transfer step was endergonic by 18.6 kcal mol^{-1}; see ESI,† Fig. S1) relative to the described pathway. A solvation model (COSMO) did not affect the turnover-limiting step.

In conclusion, we have demonstrated the reactivity of Ir^{III} piano-stool complexes with sulfonamidophosphine ligand $\mathbf{1^H}$ (METAMORPhos) for the heterolytic activation of alkyne C–H bonds. The initially generated species **2**, featuring monodentate P-coordination, reacts with exogenous base to generate complex **3**, bearing a reactive P,O-coordinated METAMORPhos ligand. In the presence of terminal alkynes, the ligand is reprotonated *via* PhC≡C–H activation to generate acetylide compound **5**. This intermolecular C–H activated species undergoes facile anti-Markovnikov hydroamination reaction in the coordination sphere of Ir^{III}. This represents a novel reaction mode for this ligand class, making this a versatile design in the context of chemically non-innocent ligand reactivity. The resulting unique four-membered Ir-PNC metallacycle **4**, featuring an exocyclic vinyl group, is structurally characterized and DFT calculations support the transient formation of an Ir^{III}-vinylidene intermediate. The insights presented potentially provide an entry into selective intra- and intermolecular C–H activation protocols with *e.g.* alkynes.

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Notes and references

‡ Crystallographic details, for **2**; $C_{32}H_{39}Cl_2IrNO_2PS$, F_w = 795.77, orange needle, 0.63 × 0.33 × 0.16 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 10.16597(16) Å,

b = 10.5116(3) Å, c = 15.5310(3) Å, α = 76.518(1)°, β = 78.361(1)°, γ = 80.796°, V = 1569.58(6) Å^3, Z = 2, D_x = 1.684 g cm^{-3}, μ = 4.57 mm^{-1}. 22 217 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. 7214 reflections were unique (R_{int} = 0.012), of which 7109 were observed [$I > 2\sigma(I)$]. 371 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0117/0.0297. R_1/wR_2 [all refl.]: 0.0120/0.0298. S = 1.091. Residual electron density between −0.68 and 0.81 e Å^{-3}. For **3**: $C_{32}H_{38}ClIrNO_2PS$, F_w = 759.31, orange block, 0.46 × 0.28 × 0.14 mm^3, monoclinic, $P2_1/n$ (no. 14), a = 14.3385(17) Å, b = 14.6511(17) Å, c = 15.2223(18) Å, β = 107.9132(17)°, V = 3042.8(6) Å^3, Z = 4, D_x = 1.658 g cm^{-3}, μ = 4.63 mm^{-1}. 45 334 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. 7021 reflections were unique (R_{int} = 0.013), of which 6806 were observed [$I > 2\sigma(I)$]. 358 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0118/0.0293. R_1/wR_2 [all refl.]: 0.0126/0.0296. S = 1.083. Residual electron density between −0.36 and 0.92 e Å^{-3}. For **4**: $C_{40}H_{44}ClIrNO_2PS$, F_w = 861.44, colorless block, 0.40 × 0.10 × 0.10 mm, monoclinic, $C2/c$, a = 22.7439(8) Å, b = 18.8669(7) Å, c = 17.5730(6) Å, β = 106.1060(15)°, V = 7244.7(4) Å^3, Z = 8, D_x = 1.580 g cm^{-3}, μ = 3.897 mm^{-1}. 40 820 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.59 Å^{-1}. 6384 reflections were unique (R_{int} = 0.0389), of which 5662 were observed [$I > 2\sigma(I)$]. 430 parameters were refined with 0 restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0226/0.0642. R_1/wR_2 [all refl.]: 0.0292/0.0707. S = 1.073. Residual electron density between −1.14 and 1.12 e Å^{-3}.

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