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Alkyne-to-Vinylidene Transformation on *trans*-(Cl)Rh(phosphine)$_2$: Acceleration by a Heterocyclic Ligand and Absence of Bimolecular Mechanism

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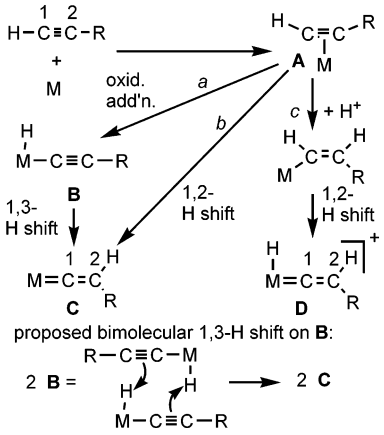
One striking advantage of metal-catalyzed processes is the profound changes in the polarity of substrates when they are coordinated to the metal. A key step in several catalytic reactions which fits this class is the transformation of a terminal alkyne (**A**, Scheme 1) to a vinylidene ligand (**C** or **D**).[1] The polarity of alkyne C1 and C2 is reversed such that C1 of the vinylidene ligand may be attacked by relatively weak oxygen nucleophiles in an anti-Markovnikov fashion.[1b,c,e,f,2] A number of groups have studied alkyne-to-vinylidene transformation on [CpRu(phosphine)$_2$]$^+$ fragments,[3] a reaction which we are studying in the context of catalytic hydration of alkynes.[2e,g]

Here we report that alkyne-to-vinylidene transformation on significantly different Rh(I) fragments (**1** to **2**, Scheme 2) is accelerated when R^1 = Ph is replaced by an imidazol-2-yl group. Previous beautiful work by Werner and co-workers[4a] showed that, in the nonheterocyclic case (**1a**, R^1 = *i*-Pr), alkyne-to-vinylidene transformation appeared to proceed in a two-step process, by way of a hydrido(alkynyl) isomer (Scheme 1, path *a*).[4] For the second step of path *a*, debate has centered on the molecularity of the 1,3-H shift:[1g] in general, for group 9 fragments, a unimolecular mechanism has been put forth,[4c] but in the case of *trans*-(Cl)M[phosphine]$_2$ (M = Rh, Ir), both a major computational study[4d] and some circumstantial evidence[4a] suggest the unusual bimolecular conversion shown at the bottom of Scheme 1. However, here we detail crossover experiments which are inconsistent with a bimolecular mechanism, regardless of whether a pendant heterocyclic base is present or not.

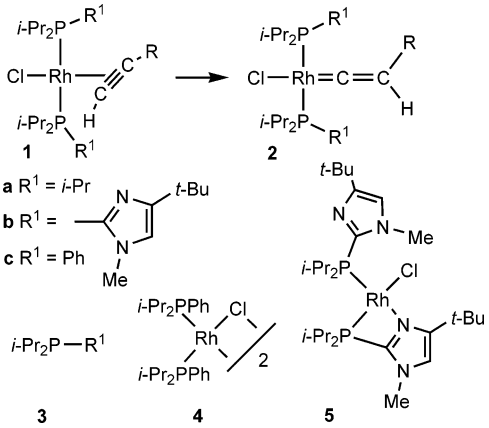
Werner's group readily isolated alkyne complexes of type **1a** in high yield and observed isomerization to vinylidene complexes **2a** within hours at 30−50 °C and also noted that the process "...lässt sich durch Zugabe von Pyridin beschleunigen" ("...may be accelerated by addition of pyridine").[4a] Our first attempt to make 1-hexyne complex **1b**−HC$_2$Bu using heterocyclic phosphine **3b** led to a surprising result: mixing 1-hexyne, [(μ-Cl)Rh(cyclooctene)$_2$]$_2$, and **3b** in molar ratio 1:0.5:2 led to the immediate and clean formation of vinylidene complex **2b**−CCHBu.[5] In fact, the reaction is essentially a titration, forming a beautiful deep permanganate-purple solution within seconds.

The obvious acceleration in formation of **2b** from **3b** relative to reported reactions using the spectator ligand **3a** prompted the more thorough study described here. For more accurate steric and electronic comparisons, **3b** and **3c** were used and cyclooctene-free materials were made to avoid any complications from the alkene ligand. Thus, mixing [(μ-Cl)Rh(cyclooctene)$_2$]$_2$ and **3c** in a molar ratio of 0.5:2 led to the formation of a purple solid in 95% yield, made by Werner et al.[6a] and formulated as dimer **4** (Scheme 2) in analogy to the purple complex from **3a** characterized by X-ray diffraction.[6b] In contrast, when **3b** was used, orange−yellow crystals of complex **5** were obtained in 95% yield. Formulation as the unsymmetrical monomer **5** with its cis-arrangement of phosphines was concluded on the basis of two ^{31}P NMR doublets, $^2J_{PP}$ = 42 Hz.

Scheme 1. Proposed Alkyne-to-Vinylidene Mechanisms



Scheme 2. Ligands and Complexes Used in This Work



Addition of 1-hexyne to either **4** or **5** in CD_2Cl_2 solution at −20 °C led to an equilibrium mixture containing the starting complex, free alkyne, and mostly the symmetrical alkyne π-complexes **1c**−HC$_2$Bu or **1b**−HC$_2$Bu, respectively, in which the alkyne complexes exhibited ^{31}P NMR doublets and diagnostic ^{1}H NMR resonances for the terminal alkyne proton.[5] With the same total concentrations of Rh and alkyne, equilibrium lay further to the side of alkyne complex in the nonheterocyclic case. Observation of these solutions at −20 °C in the NMR probe showed that the consumption of alkyne π-complex occurred 9.6 times more rapidly in the imidazole case, but the reaction order could not be determined.[5] Hydrido(alkynyl) complexes or other intermediates were not detected in these reactions.

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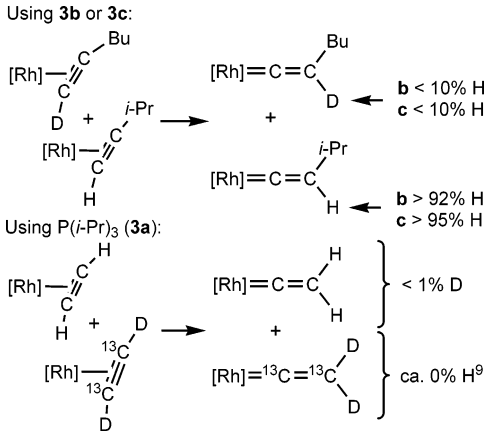
Scheme 3. Results of Crossover Experiments Forming **2**[a]



[a] Upper bounds given are estimated detection limits.

The acceleration does not appear to be a matter of an electronic effect of the heterocycle, which was probed using alkyne π-complexes **1c**− or **1b**−$H^{13}C^{13}CH$, formed from $H^{13}C^{13}CH$ and either **4** or **5** in CD_2Cl_2 at −20 °C. Analysis of the ten-line alkynyl proton AA′XX′ pattern revealed that $^2J_{CC}$ for the coordinated alkyne was identical in each case (117.0 Hz), as were the other C−H and H−H couplings within experimental uncertainty. The strong back-bonding of the metal to the alkyne π-system is obvious by noting the medium-dependent value of $^2J_{CC}$ = 166−170 Hz for acetylene itself.[7] Moreover, when the solutions of acetylene complex were allowed to warm to room temperature, **2b**− and **2c**−$^{13}C^{13}CH_2$ with $^2J_{C1-C2}$ = 58.0−58.7 Hz were seen, again consistent with the same degree of back-bonding of metal to vinylidene.[8]

In an effort to establish whether the isomerization of alkyne to vinylidene in this system is bimolecular or unimolecular, a series of double crossover experiments were performed (Scheme 3). We note that a double crossover experiment was attempted on hydrido(alkynyl)iridium species of type **B** with the P(*i*-Pr)$_3$ ligand, but rapid H−D exchange between the hydridic starting materials prevented a conclusion regarding molecularity.[4a] In our work, adding an equimolar mixture of terminal alkynes $DCC(CH_2)_3CH_3$ and $HCCCHMe_2$ (0.6 equiv of each relative to the amount of Rh) to either **4** or **5** at −20 °C produced mixtures of alkyne π-complexes **1**, which evolved to vinylidene complexes (**2**) as the mixtures were warmed. *Significantly, with an estimated detection limit of 5−10%, no crossover was detected, regardless of ligand type*, inconsistent with significant bimolecular 1,3-H shift.

However, because the propensity for bimolecular reaction could be a function of hindrance on the alkyne or the phosphine and because the previous studies[4a,d] focused on acetylene itself and the P(*i*-Pr)$_3$ ligand, we allowed a 1:1 mixture of **1a**−HCCH and **1a**−$D^{13}C^{13}CD$ to convert to vinylidene complexes **2** at 25−30 °C in C_6D_6. Remarkably, formation of **2a**−CCH_2 and **2a**−$^{13}C^{13}CD_2$ is consistent with an absence of crossover even in this system.[9] Notably, our estimated limit of detection of D in **2a**−CCH_2 is 1%.

In summary, our preliminary results show an intriguing acceleration of alkyne transformation on these square-planar Rh(I) centers by the imidazol-2-yl phosphine studied (**b** vs **c** or **a**). Of greater significance for vinylidene chemistry, in general, double crossover experiments clearly are inconsistent with significant involvement of a bimolecular mechanism for fragments derived from the three ligands studied, including P(*i*-Pr)$_3$. Future reports will attempt to clarify the mechanism of alkyne-to-vinylidene transformations in these and related systems, using a combination of experimental and theoretical approaches.

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Supporting Information Available: Details of compound preparation and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The absence of D in **2a**−CCH_2 formed from **1a** in the presence of the $D^{13}C^{13}CD$ isotopomer is the most compelling evidence against crossover. See Supporting Information for full details. Rearrangement of pure **1a**−$D^{13}C^{13}CD$ in silylated and dried NMR tubes gave **2a**−$^{13}C^{13}CD_2$ along with 10−20% of the $^{13}C^{13}CHD$ isotopomer, which complicated the analysis somewhat. In these experiments, the source of the H could not be determined, but it would not appear to be extraneous water because the amount of H incorporation was unaffected by pretreating the NMR tube with D_2O before drying, or by the presence or absence of **1a**−HCCH. Moreover, the vinylidene protons of **2**−CCH_2 did not exchange with D_2O at room temperature in C_6D_6.

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