

Insertion Reactions of Allenes Giving Vinyl Complexes

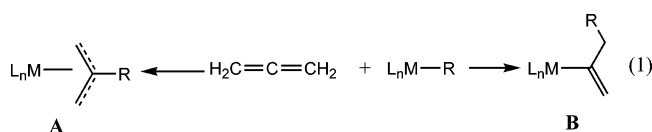
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Summary: Treatment of $\text{OsHCl}(\text{PPh}_3)_3$ with allenes $\text{CH}_2=\text{C}=\text{CHR}$ at room temperature in benzene produced the vinyl complexes $\text{OsCl}(\text{C}(\text{CH}_3)=\text{CHR})(\text{CH}_2=\text{C}=\text{CHR})(\text{PPh}_3)_2$, instead of η^3 -allyl complexes as normally observed. DFT calculations show that the formation of the vinyl complex is favored kinetically.

There has been great interest in transition-metal-catalyzed reactions of allenes.^{1,2} Insertion of allenes into $\text{M}-\text{R}$ bonds represents one of the most important fundamental steps in catalytic reactions of allenes. In principle, allenes can undergo insertion reactions with $\text{L}_n\text{M}-\text{R}$ to give either transition-metal allyl complexes **A** or vinyl complexes **B**, as illustrated in eq 1. The



insertion of allenes into $\text{M}-\text{R}$ bonds to give allyl intermediates has been frequently invoked in the mechanisms of transition-metal-catalyzed reactions of allenes. In supporting the proposed mechanisms, stoichiometric insertion reactions of allenes with $\text{L}_n\text{M}-\text{R}$ ($\text{M} = \text{Pd}(\text{II})$ or $\text{Pt}(\text{II})$,³ $\text{Rh}(\text{I})$,⁴ $\text{Ru}(\text{II})$,⁵ $\text{R} = \text{halide, H, acyl, allyl, vinyl, alkyl, aryl}$) to give transition-metal allyl com-

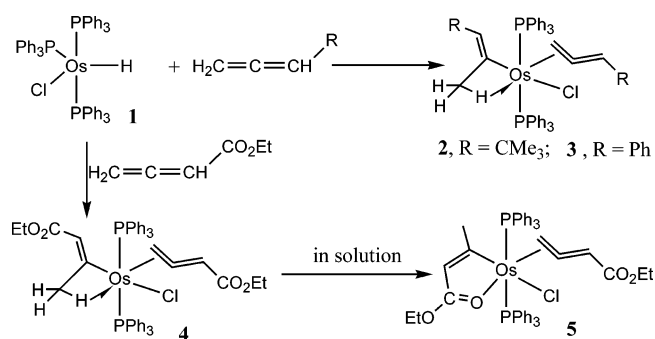
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Scheme 1



plexes are now well documented. Although catalytic reactions involving insertion of allenes into $\text{M}-\text{R}$ bonds to give vinyl intermediates were occasionally proposed,⁶ stoichiometric insertion reactions of allenes with well-defined $\text{L}_n\text{M}-\text{R}$ to give vinyl complexes cannot be found in the literature, to the best of our knowledge. In this work, we wish to report the first examples of formation of vinyl complexes from allene insertion reactions.

Treatment of $\text{OsHCl}(\text{PPh}_3)_3$ (**1**)⁷ with $\text{CH}_2=\text{C}=\text{CHCMe}_3$ at room temperature in benzene produced $\text{OsCl}(\text{C}(\text{CH}_3)=\text{CHCMe}_3)(\text{CH}_2=\text{C}=\text{CHCMe}_3)(\text{PPh}_3)_2$ (**2**) (Scheme 1). The structure of **2** has been confirmed by a single-crystal X-ray diffraction study.⁸ As shown in Figure 1, complex **2** contains an η^2 - $\text{CH}_2=\text{C}=\text{CHCMe}_3$ ligand and the vinyl ligand $\text{MeC}=\text{CHCMe}_3$, which interacts with the osmium center agostically through one of the hydrogen atoms of the α -methyl group. In agreement with the solid-state structure, the ^1H NMR spectrum showed the agostic methyl proton signal at -0.84 ppm. The chemical shift is unusually upfield for a typical CH_3 attached to an sp^2 -hybridized carbon but is close to that of the methyl group with an agostic interaction in $[\text{IrPh}(\text{C}(\text{CH}=\text{CHCMe}_3)=\text{CHCMe}_3)(\text{PMe}_3)_3]\text{PF}_6$ (-0.7 ppm).⁹ Complex **2** represents a rare example of β -agostic vinyl

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(8) See the Supporting Information for experimental and spectroscopic details of **2–6**, for X-ray studies of **2** and **5**, and for computational details.

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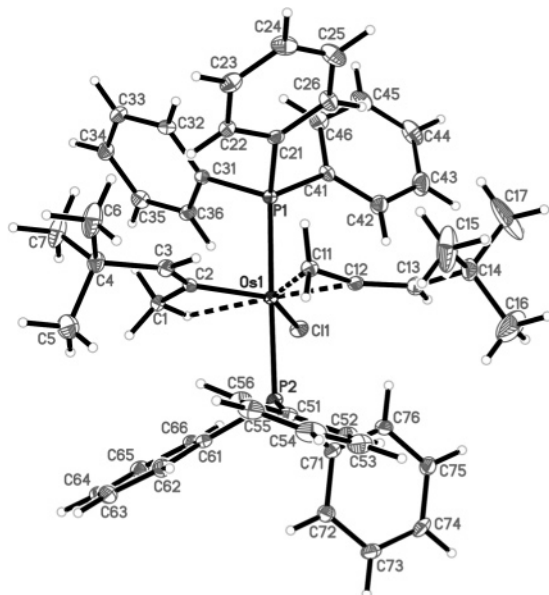


Figure 1. X-ray structure of **2**. Selected bond distances (Å) and angles (deg): Os(1)–Cl(1), 2.4570(6); Os(1)–P(1), 2.3780(6); Os(1)–P(2), 2.3646(6); Os(1)–C(1), 2.501(2); Os(1)–C(2), 2.026(2); Os(1)–C(11), 2.122(2); Os(1)–C(12), 2.044(2); C(1)–C(2), 1.498(3); C(2)–C(3), 1.332(4); C(11)–C(12), 1.428(3); C(12)–C(13), 1.321(3); C(11)–C(12)–C(13), 142.9(2).

complexes.¹⁰ β -Agostic vinyl complexes are interesting, as they can be regarded as the resting states for the interconversion of allene and vinyl complexes.¹¹

The vinyl ligand MeC=CHCMe₃ in **2** is derived from insertion of CH₂=C=CHCMe₃ into an Os–H bond. A number of allene insertion reactions have been reported, for example, in the reactions of allenes with complexes such as [MR(sol)(L–L)]⁺ (M = Pt, Pd; L = nitrogen, or sulfur or phosphorus donors),³ RhH(L)(PPh₃)₃ (L = CO, PPh₃),⁴ RuHCl(CO)(PPh₃)₃,^{5a} and RuH(NO)(PPh₃)₃.^{5b} In all these reported reactions, the isolated products are allyl complexes. Thus, the formation of complex **2** from the reaction of **1** with CH₂=C=CHCMe₃ is interesting and unexpected, as it represents the first example of formation of vinyl complexes from allene insertion reactions.

To see if the reactions are general, we have studied the reactions of OsHCl(PPh₃)₃ with other allenes. Reaction of OsHCl(PPh₃)₃ with CH₂=C=CHPh produced the analogous complex OsCl(C(CH₃)=CHPh)(CH₂=C=CHPh)(PPh₃)₂ (**3**), which was previously obtained from the reaction of OsHCl(PPh₃)₃ with excess PhC≡CCH₃.¹² Similarly, reaction of OsHCl(PPh₃)₃ with CH₂=C=CHCO₂Et produced the insertion product OsCl(C(CH₃)=CHCO₂Et)(CH₂=C=CHCO₂Et)(PPh₃)₂ (**4**) (Scheme 1). The structure of **4** must be similar to that of **2**, as inferred from its NMR spectroscopic data. It is found that complex **4** is unstable in solution. At room temperature,

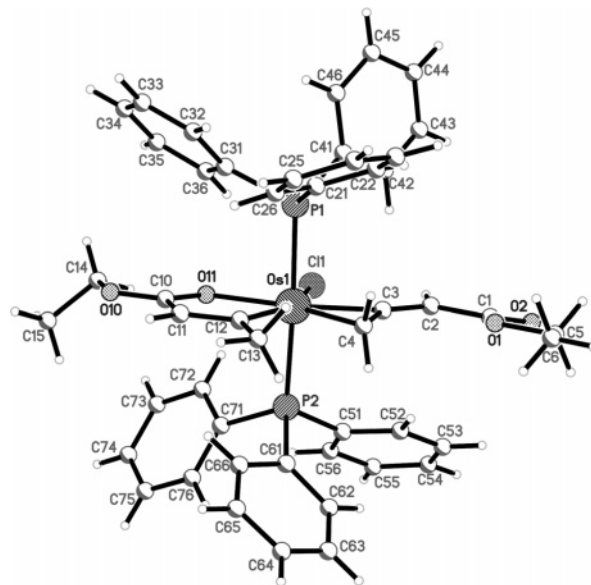


Figure 2. X-ray structure of **5**. Selected bond distances (Å) and angles (deg): Os(1)–Cl(1), 2.4511(7); Os(1)–P(1), 2.3801(8); Os(1)–P(2), 2.4142(8); Os(1)–C(3), 2.405(3); Os(1)–C(4), 2.416(3); Os(1)–C(12), 2.078(3); Os(1)–O(11), 2.144(2); C(3)–C(4), 1.367(5); C(2)–C(3), 1.336(5); O(11)–C(10), 1.261(4); C(10)–C(11), 1.416(5); C(11)–C(12), 1.363(5); C(12)–C(13), 1.504(4); C(2)–C(3)–C(4), 142.6(3).

it slowly isomerized to complex **5**, in which the vinyl ligand is chelated to osmium through a C atom and an O atom. The structure of **5** has been confirmed by X-ray diffraction (Figure 2). The solution NMR data are fully consistent with the solid-state structure.

The reactions described above demonstrate that allenes with either electron-donating or -withdrawing groups undergo insertion reactions with OsHCl(PPh₃)₃ at the less substituted C=C bond to give vinyl complexes instead of η^3 -allyl complexes, as normally observed. To understand why allyl complexes were not produced in the reactions of OsHCl(PPh₃)₃, we have studied the formation of vinyl versus η^3 -allyl complexes from the model reaction of OsHCl(PH₃)₃ with H₂C=C=CH₂ by density functional theory calculations.⁸ Figure 3 shows the potential energy profiles for the two insertion pathways leading to the formation of the vinyl (**PR-vinyl**) and allyl (**PR-allyl**) model complexes. The results indicate that the formation of the vinyl complex is kinetically favorable. Thermodynamically, the vinyl complex is less stable than the η^3 -allyl complex. The very high barrier for the reverse process, **PR-vinyl** → **PC-vinyl**, prevents the formation of the thermodynamically favored η^3 -allyl (**PR-allyl**) complex. Therefore, once **PR-vinyl** is formed, it is stable enough to be isolated. The important implication of the results is that, although vinyl complexes may be in general thermodynamically less stable than η^3 -allyl complexes (in view of the dominant allyl complexes in the literature), formation of vinyl complexes can still be kinetically possible. OsHCl(PPh₃)₃ provides an opportunity for such a possibility to be realized. To check the reliability of the relative energies presented in Figure 3, which were evaluated on the basis of the gas-phase model calculations, we examined the solvation effects by doing single-point solvation energy calculations with the polarizable continuum models (PCM).⁸ The results of the PCM

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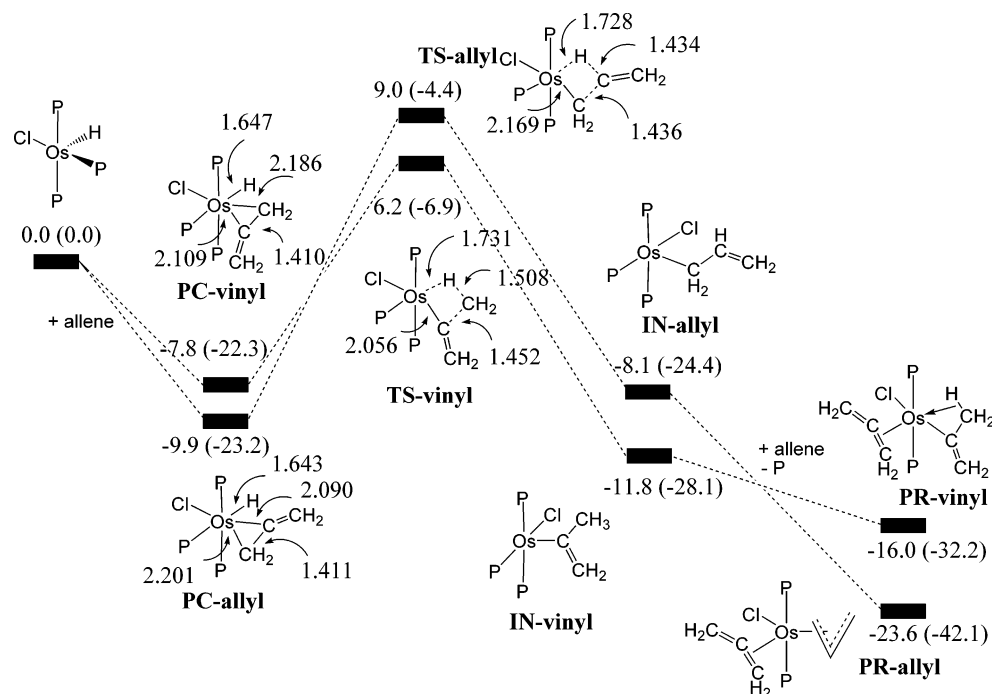


Figure 3. Energy profiles for the two possible insertion pathways in the reaction of $\text{OsHCl}(\text{PH}_3)_3$ with allene. In all of the structures, P stands for PH_3 . The relative free energies and reaction energies (in parentheses) are given in kcal/mol. In calculating the relative energies, we included the energies calculated for free $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ and PH_3 whenever necessary in order to make the energies comparable for all the species.

calculations show that the changes in the relative energies are within 0.3 kcal/mol when the solvation energies are included (see the Supporting Information for more details).

Figure 3 also shows the key structural features of the calculated structures of the allene-coordinated precursor complexes (**PC-vinyl** and **PC-allyl**) and the insertion transition states (**TS-vinyl** and **TS-allyl**). The Os–H bond distances in the two precursor complexes are approximately the same. In both the two precursor complexes, the distance between the metal center and the central carbon of the η^2 -allene ligand is noticeably shorter than that between the metal center and the terminal π -bonded allenic carbon. The insertion reactions involve the breaking of an allenic Os–C bond and an Os–H bond and the formation of a new C–H bond. From **PC-vinyl** to **TS-vinyl**, the weaker allenic Os–C bond in **PC-vinyl** is the one being stretched. From **PC-allyl** to **TS-allyl**, the stronger allenic Os–C bond in **PC-allyl** is the one being stretched. Thus, the insertion occurs more easily from the precursor complex **PC-vinyl** leading to the formation of the vinyl product **PR-vinyl** in comparison with that from **PC-allyl**. For many other allene complexes, the bond between the metal center and the central carbon of the η^2 -allene ligand was also found to be generally shorter than that between the metal center and the terminal π -bonded allenic carbon.^{3j} However, there has been no report of observing the relevant vinyl products from their insertion reactions.

We are now doing more calculations in order to gain better insight into this important issue.

In summary, allenes undergo insertion reactions with $\text{OsHCl}(\text{PPh}_3)_3$ to give vinyl complexes instead of η^3 -allyl complexes. These are the first examples of formation of vinyl complexes from allene insertion reactions with well-defined metal complexes. The formation of the vinyl complex was found to be kinetically favorable. From this study, we see that it is possible to tune the properties of $\text{L}_n\text{M}-\text{R}$ so that they undergo insertion reactions with allenes to give vinyl complexes rather than allyl complexes and that new metal catalysts can be designed to catalyze insertion reactions of allenes via a vinyl intermediate. We are currently studying other systems to further understand factors controlling the formation of vinyl or allyl complexes.

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Supporting Information Available: Text and tables giving experimental procedures, characterization data, and Cartesian coordinates of the calculated structures and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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