

X-ray, ^{13}C NMR, and DFT Studies on a Ruthenium(IV) Allyl Complex. Explanation for the Observed Control of Regioselectivity in Allylic Alkylation Chemistry

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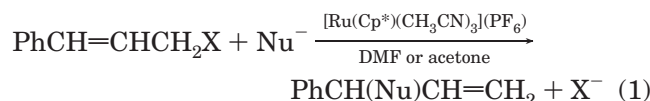
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Received December 1, 2004

Summary: X-ray, ^{13}C NMR, and DFT studies on the cationic Ru(IV) allyl complex $\text{Ru}(\text{Cp}^*)\text{Cl}(\text{CH}_3\text{CN})(\eta^3\text{-PhCHCHCH}_2)$, as a PF_6 salt, have revealed a marked asymmetry in the bonding of the allyl ligand, which can be interpreted as arising from differences in π -bonding from the metal center to the two terminal allyl carbons. This asymmetry in the bonding is offered as an explanation for the observed control of regioselectivity in the Ru-catalyzed allylic alkylation reaction.

The Ru-catalyzed allylic alkylation reaction has attracted significant interest due to its recognized regioselectivity in favor of branched products.¹ The most commonly used catalyst precursor contains a Cp or Cp* ligand.^{2,3} Trost and co-workers¹ have reported that $[\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3](\text{PF}_6)$ (**1**) is an excellent catalyst for this reaction and, specifically, that reaction of the allyl substrate $\text{PhCH}=\text{CHCH}_2\text{X}$ (**2**; X = halogen or carbonate) with either a carbon or nitrogen nucleophile, Nu^- , preferentially affords the branched product $\text{PhCH}(\text{N})\text{-CH}=\text{CH}_2$ (see eq 1). When the branched starting mate-



rial $\text{PhCH}(\text{X})\text{CH}=\text{CH}_2$ is used as substrate, the reaction is thought to proceed with retention of configuration at the methine carbon atom, i.e., with inversion in both of

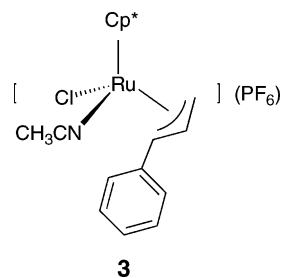
(1) (a) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813–5837. Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943. (b) Trost, B. M.; Rudd, M. T. *Org. Lett.* **2003**, *5*, 1467–1470. (c) Trost, B. M.; Fraise, P. L.; Ball, Z. T. *Angew. Chem., Int. Ed.* **2003**, *41*, 1059–1061. (d) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544–2546.

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the presumed mechanistic steps.¹ It is not immediately clear why the branched isomer is formed, although, in contrast to related Pd(II) chemistry,⁴ the product is clearly not formed under steric control. We offer here an explanation for this selectivity based on X-ray, NMR, and computational studies.

Since this allylation reaction is thought to proceed via a Ru(IV) allyl intermediate,² we have prepared the allyl complex **3** in 94% yield by a stoichiometric reaction of **2** (X = Cl) with **1**.⁵ Complex **3** reacts quantitatively with



morpholine after extraction of chloride with AgPF_6 to afford both the branched and linear isomeric organic products in a 95:5 ratio.

(4) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681–1687. Pfaltz, A.; Prétôt, R., A. *Angew. Chem.* **1998**, *110*, 337–339 and references therein.

(5) $[\text{RuCp}^*\text{Cl}(\eta^3\text{-phenylallyl})\text{CH}_3\text{CN}]\text{PF}_6$ (**3**): *trans*-cinnamyl chloride (136 μL , 0.963 mmol, 1.2 equiv) was added to a stirred solution of $[\text{RuCp}^*(\text{CH}_3\text{CN})_3]\text{PF}_6$ (405 mg, 0.803 mmol) in 5 mL of CH_2Cl_2 , and the resulting clear solution was stirred at room temperature overnight. The solution volume was reduced under vacuum to 1 mL, and diethyl ether was added, precipitating a red powder. The solid was washed with diethyl ether (2×5 mL) and dried under vacuum to yield 434 mg (94%) of product. Crystals suitable for an X-ray structure determination were obtained by layering Et_2O in a CH_2Cl_2 solution of **3**. Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{NF}_6\text{PClRu}$: C, 43.87; H, 4.73; N, 2.44. Found: C, 43.01; H, 4.53; N, 1.85. HR-MALDI MS: m/z 389.1, 355.1, 315.1. There is precedence for this type of reaction; see: Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2004**, *23*, 3763–3765.