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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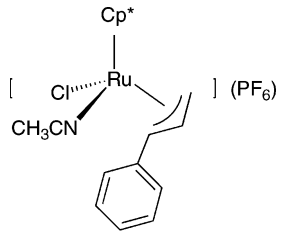
Summary: X-ray, ^{13}C NMR, and DFT studies on the cationic Ru(IV) allyl complex Ru(Cp)Cl(CH_3CN)(η^3-PhCHCHCH$_2$), as a PF_6 salt, have revealed a marked asymmetry in the bonding of the allyl ligand, which can be interpreted as arising from differences in π-bonding from the metal center to the two 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-workers[1] have reported that [Ru(Cp*)(CH_3CN)$_3$](PF_6) (**1**) is an excellent catalyst for this reaction and, specifically, that reaction of the allyl substrate PhCH=CHCH$_2$X (**2**; X = halogen or carbonate) with either a carbon or nitrogen nucleophile, Nu^-, preferentially affords the branched product PhCH(N)-CH=CH$_2$ (see eq 1). When the branched starting material PhCH(X)CH=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 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.

$$\mathrm{PhCH{=}CHCH_2X + Nu^-} \xrightarrow[\text{DMF or acetone}]{[\mathrm{Ru(Cp^*)(CH_3CN)_3](PF_6)}} \mathrm{PhCH(Nu)CH{=}CH_2 + X^-} \quad (1)$$

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.



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(5) [RuCp*Cl(η^3-phenylallyl)CH_3CN]PF_6 (**3**): *trans*-cinnamyl chloride (136 μL, 0.963 mmol, 1.2 equiv) was added to a stirred solution of [RuCp*(CH_3CN)$_3$]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 $C_{21}H_{27}NF_6PClRu$: 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.

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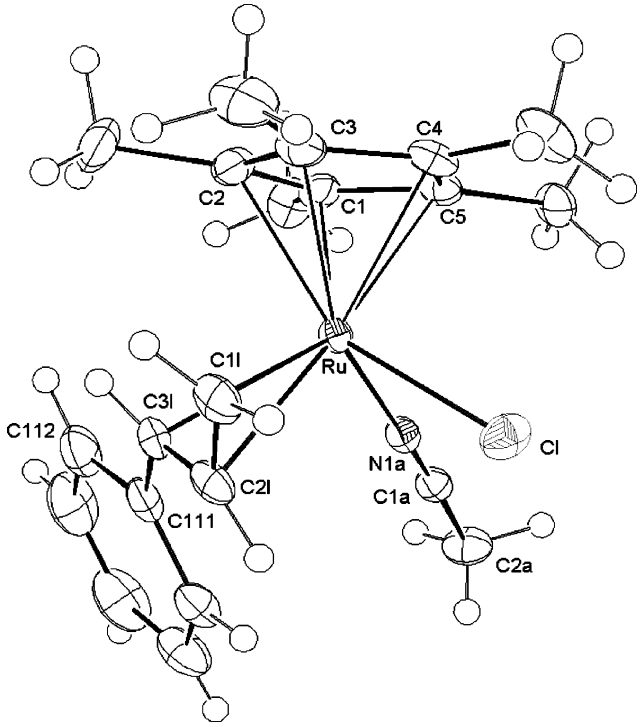
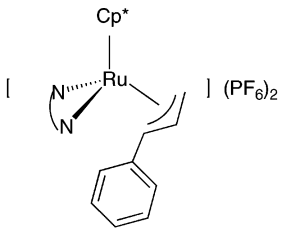


Figure 1. ORTEP view of the cation of salt **3** showing 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Ru−N(1A), 2.065(2); Ru−Cl, 2.3998(7); Ru−C(1L), 2.192(3); Ru−C(2L), 2.162(3); Ru−C(3L), 2.351(2); Ru−C(1), 2.181(3); Ru−C(2), 2.221(3); Ru−C(3), 2.248(3); Ru−C(4), 2.263(3); Ru−C(5), 2.191(3); N(1A)−Ru−Cl, 82.25(6).

The solid-state structure for **3** was determined by X-ray diffraction methods,[6] and an ORTEP view of this cation is shown in Figure 1, with selected geometrical parameters given in the caption. The immediate coordination sphere consists of the Ru atom surrounded by the Cp*, the η^3-allyl ligand, one complexed acetonitrile, and the coordinated chloride ion. The most interesting aspect of this structure involves the two markedly different terminal Ru−C bond distances, Ru−C1L and Ru−C3L, at 2.192(3) and 2.351(2) Å, respectively. Obviously the two terminal C atoms, the possible candidates for attack by the nucleophile, Nu^-, are quite different, with the Ru−C3L bond being especially long. Routine Ru−C allyl separations are on the order of 2.1−2.2 Å.[7] We note that Bruneau and co-workers[7d] have found similar values in their structure of the Ru(Cp*)-(phenanthroline) dicationic complex **4**.



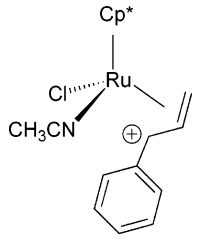
4, N,N = 1,10-phenanthroline

In **3** the relatively slender acetonitrile is proximate to the phenyl group of the allyl ligand, although there are no especially close contacts between these two. On the basis of the structure of **3** this allyl complex is open to attack by a nucleophile from the back side.

In the solid state the molecule exists as the isomer shown; however, an acetone solution prepared from the recrystallized material reveals three species in the ratio 78:19:3 (see Chart 1). A solution prepared from the product as a powder clearly reveals the same three species (in the ratio 55:14:31), but the minor component is now more abundant. An acetone solution containing 1 equiv each of **1** and **2** (X = Cl) showed four allyl species.[8] We believe these three complexes are due to the presence of exo and endo isomers, i.e., the central CH bond can point toward or away from the Cp* and there is an interchange of the allyl relative to the positions of the complexed acetonitrile and chloride ligands.[8]

The ^{13}C and ^1H chemical shifts for the allyl carbons of all three isomers are shown in Chart 1 and have been determined using a mixture of two-dimensional NMR methods. The major isomer (endo) is that found in the solid state on the basis of NOE experiments. The resonances for the methylene carbon C1 are all found at rather normal positions[7a,b] for a Ru−allyl complex: ca. 59−68 ppm. However, the resonance positions for the methine carbon C3 are found at much higher frequency: ca. 91−103 ppm. These chemical shift data suggest much less π back-bonding from the metal center to this terminal carbon and thus a relatively more electrophilic carbon center.

We considered the possibility that a resonance structure such as **5** might be a contributor. This would be a



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Ru(II) (and not Ru(IV)) cation with the charge localized on carbon C3. It would fit the observed Ru−C1L and Ru−C2L bond lengths.[7] However, one might expect some delocalization of the positive charge into the phenyl ring if C3 was strongly positive. For all three isomers the para carbon signals appear at ca. 129.5−130.5 ppm, i.e., in routine positions, so that we do not

(6) (a) Crystallographic data for **3**: $C_{21}H_{27}ClF_6NPRu$, fw = 574.93, monoclinic, space group $P2_1/c$ (No. 14), a = 11.8085(13) Å, b = 15.1804(17) Å, c = 13.4054(16) Å, β = 104.605(4)°, V = 2325.4(5) Å^3, Z = 4, D_c = 1.642 g cm^{-3}, Mo Kα radiation, λ = 0.710 73 Å, μ = 9.14 cm^{-1}, T = 120(2) K. A total of 20 762 reflections were collected on a Bruker SMART CCD diffractometer in the range $2.98 \le \theta \le 26.01°$. A total of 4556 unique reflections, after corrections for *Lp* and absorption, were used for the solution and refinement (based on F_o^2) of the structure. All non-H atoms were refined anisotropically. Hydrogen atoms, in their calculated positions, were included in the refinement using a riding model. The final R factor is 0.0272 for 3712 observed reflections and 0.0398 for all data.

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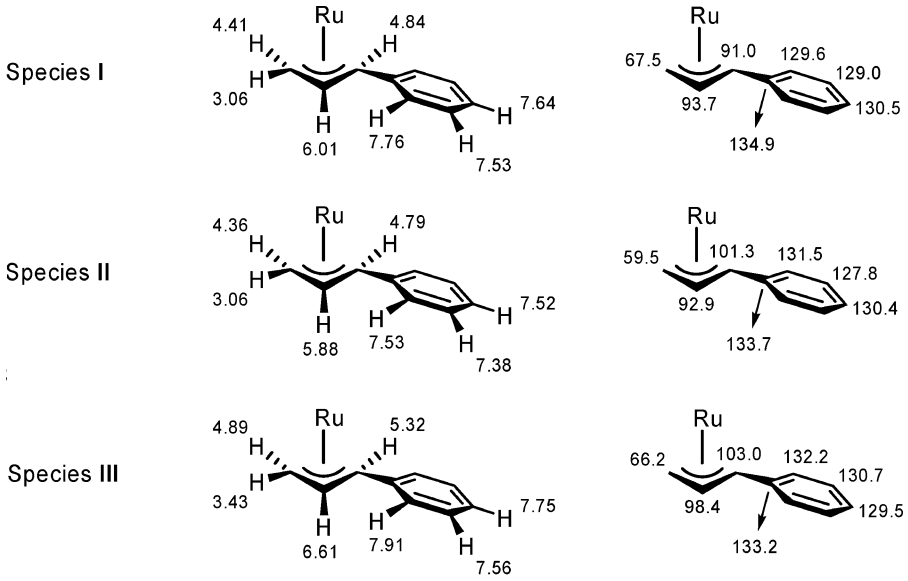
(8) There is an additional 2 equiv of acetonitrile and/or acetone which may be involved as ligands for the fourth species.

Chart 1. ^{13}C and ^{1}H Allyl Chemical Shifts for the Three Isomers of 3 in Acetone Solution[a]



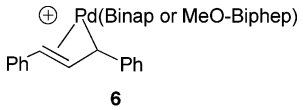
Ratio I:II:III in the crystal solution 78:19:3

Ratio I:II:III in the powder solution 55:14:31

[a] Species **I** corresponds to the X-ray structure. Species **II** is thought to have the allyl phenyl proximate to the chloride ligand and an endo allyl structure.

favor a structure with significant carbonium-ion character.

In earlier X-ray and ^{13}C NMR studies[9] involving the palladium cation Pd(1,3-diphenylallyl)(Binap or MeO−Biphep)$^+$ (**6**), we suggested that an allyl resonance structure of the type shown might be an important contributor to the ground-state structure. In **3**, we



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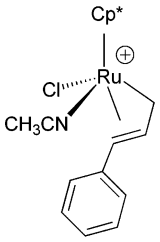

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cannot completely exclude a contribution from an "enyl" structure, i.e., **7**, since the observed allyl ^{13}C chemical shifts would fit this suggestion; however, we note that (1) the separations C1L−C2L and C2L−C3L at ca. 1.415(4) and 1.412(4) Å, respectively, are identical within the experimental error (see the Supporting Information) and (2) the relatively short Ru−C2L bond length, 2.162(3) Å, which is even shorter than the Ru−C1L distance, 2.192(3) Å, is not in keeping with **7**.

The simplest structural solution remains that of a distorted Ru(IV) π-allyl ligand in which the bonding is rather asymmetric, and to test this, we have carried out DFT calculations[10] on a model complex, [Ru(η^5-Cp)Cl(CH$_3$CN)(η^3-PhCHCHCH$_2$)] (**3′**), differing from the real molecule, **3**, by the replacement of the Cp* by the smaller Cp. The optimized structure of **3′** is depicted in Figure 2a. It compares reasonably well with the experimental X-ray structure for **3**, although the Ru−X distances in the model are a bit on the long side (mean and maximum absolute deviations of 0.05 and 0.14 Å, respectively). The overall geometry of the model reproduces the experimental structure, as shown by the Cp−Ru−L angles, with the mean and maximum absolute deviations between optimized and experimental Cp−Ru−L angles of 1 and 4°, respectively.

The calculations reproduce the geometric distortion of the allyl ligand observed in the X-ray structure of **3** reasonably, namely, the bond length Ru−C3L is 0.26 Å longer than Ru−C1L in the optimized model, **3′**. The electronic nature of this difference is confirmed by the corresponding Wiberg indices,[11] which are well-known bond strength indicators and are more reliable than distances. The calculated values for these indices (Figure 2b) show a stronger bond between the metal and C1L (0.459), compared to Ru−C3L (0.319). The relevance of the Wiberg indices for evaluating bond strengths is demonstrated by the value for the Ru−C2L bond (0.243). Despite the similar bond distances Ru−C1L and Ru−C2L, the latter is the weakest of the

(9) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35−68. Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727−734. Barbaro, P.; Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. W. *Organometallics* **1995**, *14*, 5160−5170. Pregosin, P. S.; Ruegger, H.; Salzmann, R.; Albinati, A.; Lianza, F.; Kunz, R. W. *Organometallics* **1994**, *13*, 83−90. Barbaro, P.; Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. W. *Organometallics* **1995**, *14*, 5160.

(10) DFT calculations were performed with the Gaussian 98 software package using the B3LYP hybrid functional with a LanL2DZ basis set augmented with a polarization function for Ru and Cl and a 4-31G(d) basis set for the other atoms. Computational details and the corresponding list of references are given as Supporting Information.

(11) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083;

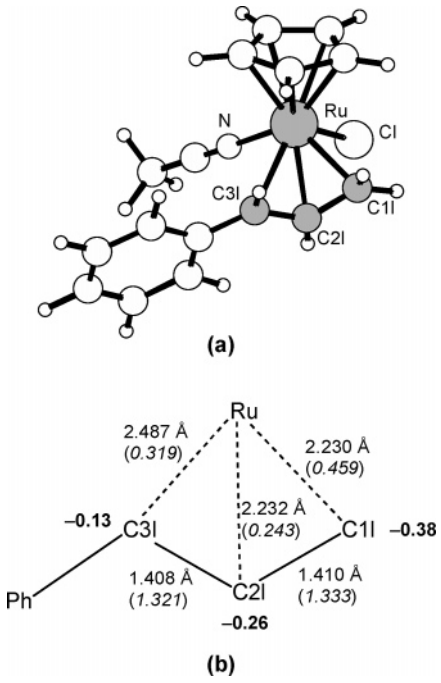

Figure 2. (a) Optimized geometry (B3LYP) of [Ru(η^5-Cp)Cl(CH_3CN)(η^3-PhCHCHCH_2)]. Ru and the allylic carbon atoms are shaded. (b) Bond distances (Å), Wiberg indices (in italics), and NPA charges (in boldface) relevant for the allylic coordination to Ru.

three Ru−C(allyl) bonds. This is expected, given the nodal characteristics of the orbitals of a coordinated allyl, specifically π_2, with no contribution from the central carbon. The differences between the Ru−C1L and Ru−C3L terminal bonds in the allylic ligand can be assigned to less efficient back-donation from the metal to C3L and are reflected in the charges calculated by means of a natural population analysis (Figure 2b). They show an electron poorer C3L, in comparison with either C1L or C2L. This result corroborates the ^{13}C NMR data, discussed above.

The difference between the bond strengths of the two terminal bonds (Ru−C3L and Ru−C1L) in **3′**, i.e., the *distortion* on the coordination of the allyl ligand, can also be related to the orbital interactions between the metal and the ligand. This is illustrated by the HOMO-6 of the molecule (Figure 3a), showing a much stronger bonding interaction between the metal and C1L relative to the metal and C3L.

Further, the implications from the discussion above, with respect to the position of the nucleophilic attack, are reinforced by the nature of the LUMO (Figure 3b), which demonstrates a relatively large contribution at C3L. The orbital picture is, therefore, completely consistent with attack by a nucleophile at the less negative (but not positive) C3L allyl carbon atom.

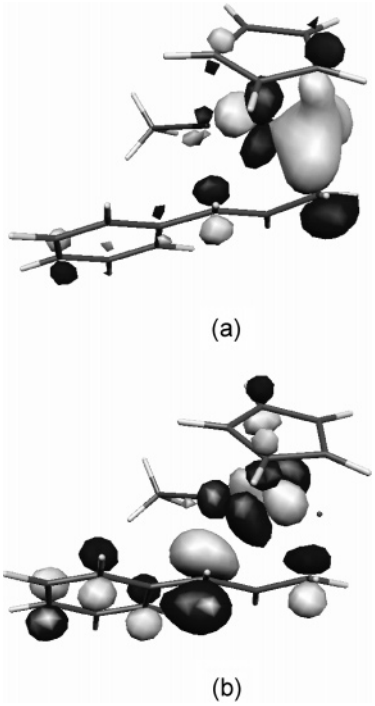

Figure 3. (a) View of the HOMO-6 of cation **3′** showing the differences in bonding between the Ru−C bonds involving the two terminal carbons of the allyl ligand. (b) Representation of the LUMO of **3′**, revealing the importance of the contribution on C3L, the preferred location of nucleophilic attack.

In conclusion, on the basis of crystallography, NMR and calculations, we find that a geometrically and electronically distorted allyl ligand is the source of the observed control of regioselectivity in the Ru(II)-catalyzed allylic alkylation reaction.

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Supporting Information Available: Text and a table giving computational details and a CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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