Ab Initio Molecular Orbital Study on Rhodium(I)-Catalyzed Isomerization of Allylic Amines to Enamines

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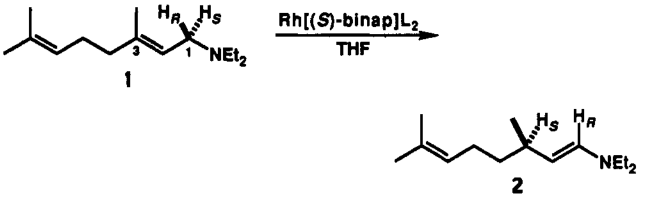
Summary: **Molecular orbital calculations suggest that the square-planar $[Rh(PH_3)_2(NH_3)(CH_2{=}CHCH_2NH_2)]^+$ complex is transformed to $[Rh(PH_3)_2(NH_3)((E)\text{-}CH_3CH{=}CHNH_2)]^+$ via intramolecular oxidative addition of the C(1)–H bond to the Rh(I) center, giving a distorted-octahedral Rh(III) hydride intermediate, followed by reductive elimination accompanied by allylic transposition.**

Cationic (*S*)-BINAP–Rh(I) complexes[1] catalyze the highly enantioselective isomerization of diethylgeranylamine (1) to citronellal (*R*,*E*)-enamine 2, which serves as a key step in the industrial production of (–)-menthol.[2,3]



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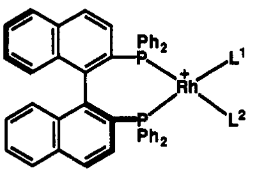
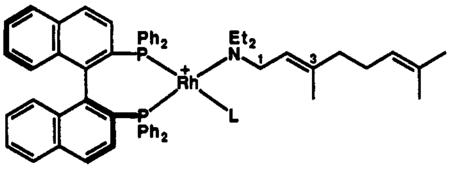
2



3, L^1, L^2 = THF, acetone, diene, etc.
4, L^1-L^2 = η^3-2
5, L^1 = L^2 = N-coordinated 2



6, L = oxygen- or nitrogen-donor molecule

Scheme I. Direct Mechanism

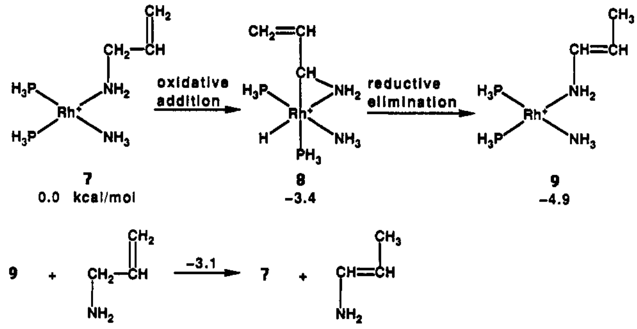
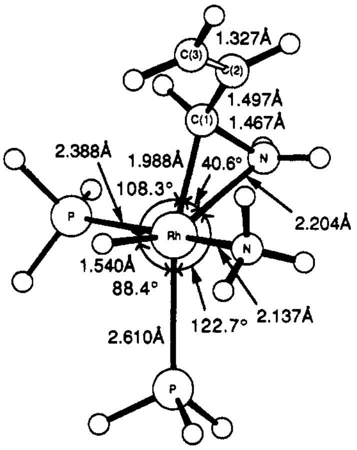


Chart I. Optimized Structure of 8



The 1,3-hydrogen shift occurs in a suprafacial manner with strict differentiation between the *pro-S* and *pro-R* hydrogens at C(1) of the allylic amine 1. Any BINAP–Rh complexes of type 3–5 act as catalysts or catalyst precursors of this isomerization. The reaction has been proven to start with the Rh(I)–allylamine complex 6, in which only the nitrogen atom interacts with the Rh center, leaving the olefinic bond intact. The activation of the C(1)–H bond has been considered to occur by direct means in the 16-electron complex 6[4] or by a dissociative mechanism involving the loss of L.[3] The catalytic reaction is very efficient, and only enamine complexes 4 and 5 are detectable during the reaction. As such, we were interested in performing the ab initio MO calculations on the model systems to infer the exact reaction pathway as well as the nature of the undetectable, short-lived intermediates. The results basically support the operation of the direct mechanism but require modifications of the details of the original postulate (C–H oxidative addition to Rh instead of metal hydride β-elimination).[4]

First, cationic $Rh(PH_3)_2(NH_3)(CH_2{=}CHCH_2NH_2)$ (7) was taken as a simple model of 6 for the direct C–H activation (Scheme I). For each structure a full geometry

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(1) Noyori, R. *Science* **1990**, *248*, 1194. Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. Noyori, R. *CHEMTECH* **1992**, *22*, 360.

(2) Tani, K.; Yamagata, T.; Otsuka, S.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R. *J. Chem. Soc., Chem. Commun.* **1982**, 600. Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. Otsuka, S.; Tani, K. *Synthesis* **1991**, 665.

(3) Inoue, S.-I.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 4897.

(4) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187.

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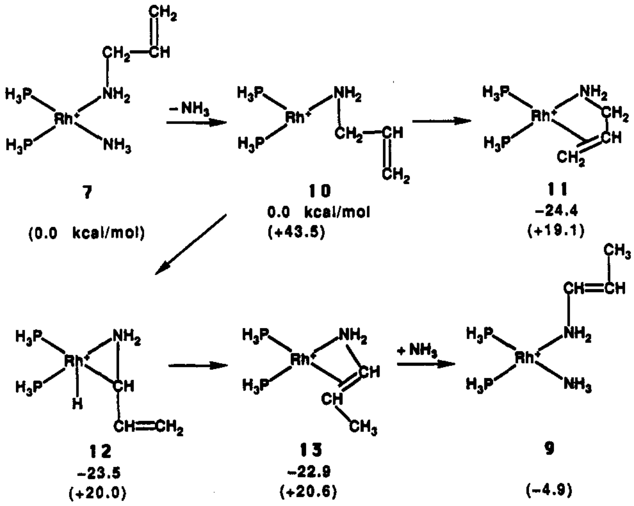
optimization was carried out at the restricted Hartree–Fock level using energy gradient techniques and a restricted second-order Møller–Plesset calculation was performed for the resulting local minimum geometry.[5,6] In the square-planar Rh complex 7, the allylamine has a syn-eclipsed conformation as in the free state. Its conversion to the distorted-octahedral Rh(III) hydride 8 (∠C-Rh-N = 40.6°) appears to be exothermic by 3.4 kcal/mol. The hydride on the Rh(III) center is then delivered directly to the C(3) terminus to give the square-planar (*E*)-enamine–Rh(I) complex 9, in which the olefinic bond does not interact with Rh. Thus, the two-step transformation 7 → 8 → 9 is best viewed as an intramolecular oxidative addition of the C(1)–H bond to the Rh(I) center, giving the alkyl–Rh(III) hydride species, followed by an intramolecular reductive elimination accompanied by allylic transposition. The overall reaction of the Rh complex is exothermic by 4.9 kcal/mol, and this value should be compared with the increase in stability, 8.0 kcal/mol, from free allylamine to (1*E*)-propenylamine. Thus, the ligand exchange between the chain-carrying enamine complex 9 and allylamine, generating the allylamine complex 7 and the free enamine, occurs with a 3.1 kcal/mol preference.

The structure of 8 is noteworthy (Chart I). Removal of a hydride from alkylamines forms the corresponding iminium ions, whose coordination to transition metals gives either π complexes or σ-bonded three-membered cycles.[7] Ligation of the cationic dehydroallylamine to Rh(I) is aided by substantial electron donation from the metal to the electron-deficient C(1) atom, resulting in the Rh(III) complex 8, which possesses a covalent C–Rh bond and an N–Rh dative bond. This view is consistent with the structural characteristics, particularly the octahedral geometry, a long C–N bond (1.467 Å), a small H–C(1)–N–C(2) dihedral angel (124.6°), and noncoplanarity of the C(2)=C(3) bond and a possible C(1)=NH_2 plane (twist angle ca. 30°). Notably, the organic moiety in 8 as well as the allylamine ligand in 7 have an s-trans conformation with respect to the N–C(1) and C(2)–C(3) bonds, allowing the overall suprafacial 1,3-hydrogen shift 7 → 9.

We then examined the possibility of the dissociative mechanism for the C(1)–H activation in which Rh maintains the same +1 oxidation state throughout the reaction. A 14-electron, T-shaped d^8 metal complex is involved in analogous β-elimination of $M(PH_3)(H)(C_2H_5)$ (M = Ni, Pd) to $M(PH_3)(H)_2(C_2H_4)$[8] as well as olefin insertion into a $(PH_3)_2Pt$–H bond.[9,10] The methylene group in tricoordinate $Rh(PH_3)_2(CH_2{=}CHCH_2NH_2)$ (10) (Scheme II) is placed in its P–Rh–P plane to cause weak H/Rh interactions. However, the expected β-hydride elimination utilizing the vacant coordination site does not occur. Instead, the tricoordinate complex tends to form the stable chelate allylamine complex 11, which is unreactive because of the unsuitable Rh/C–H geometrical arrangement. In addition, the T-shaped species can be transformed to various Rh(III) complexes having distorted-square-pyramidal structures. The C–H oxidative-addition processes (instead of β-elimination), occurring via a substantial geometrical change of 10, are highly exothermic. The tricoordinate species 10 forms a pentacoordinate Rh(III) hydride complex, whose structure resembles that of 8 except for the absence of the NH_3 ligand (−14.0 kcal/mol relative to 10). Alternatively, 10 may lead to the stereoisomeric, thermodynamically more favored complex 12 (−23.5 kcal/mol). The Rh(III) intermediate 12 is then transformed via reductive elimination to the tetracoordinate η^3-enamine–Rh(I) complex 13, in which the olefinic ligand is easily displaced by NH_3 to produce 9. However, the operation of such dissociative mechanisms is unlikely, because the requisite tricoordinate Rh species 10, generated from 7, exists in very low concentration; dissociation of NH_3 from 7 was calculated to be endothermic by 43.5 kcal/mol.

Scheme II. Dissociative Mechanism[a]



[a] Energies are based on that of 10, while the values in parentheses are relative to the energy of 7.

On the basis of the MO calculations coupled with earlier experimental findings,[2,3] we can now conclude that the Rh(I)-catalyzed 1,3-hydrogen shift reaction 1 → 2 proceeds via a nitrogen-triggered mechanism involving Rh(I)/Rh(III) two-electron-exchange processes. In the actual catalytic reaction with a high substrate/catalyst ratio, the reaction starts from the undetectable tetracoordinate Rh(I)–amine complex 6 (L = N-coordinated 2) formed by the turnover-limiting reaction between 1 and 5. The C(1)–H bond cleavage occurs directly from 6 via intramolecular oxidative addition rather than β-elimination of the Rh^I–H element after dissociation of 2. The intermediate is a hexacoordinate Rh(III) hydride species possessing a three-membered, cyclometalated structure analogous to 8. This intermediate causes hydrogen movement from the Rh(III) center to the C(3) position via reductive elimina-

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(5) The calculations were carried out at the Computer Centers of the Institute for Molecular Science and Kinjo Gakuin University using GAUSSIAN 86 (Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian 86; Carnegie-Mellon Quantum Chemistry Publishing Unit, Carnegie-Mellon University: Pittsburgh, PA 15213, 1986. McMurchie, L. E.; Davidson, E. R. *J. Comput. Phys.* **1981**, *44*, 289. Martin, R. L. Unpublished report) and GAUSSIAN 88 (Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. GAUSSIAN 88; Gaussian, Inc.: Pittsburgh, PA, 1988).

(6) The basis set used for Rh is a relativistic effective-core potential and a split-valence basis set (Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270); for other atoms a 6-31G split-valence basis set is used (Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257).

(7) Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100. Plössl, K.; Norton, J. R.; Davidson, J. G.; Barefield, E. K. *Organometallics* **1992**, *11*, 534.

(8) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

(9) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(10) For stable tricoordinate Rh(I) complexes, see: Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183.

tion, giving back the square-planar Rh(I) complex 5. The enantioselection is made at the cyclometalation step, and the atomic arrangement postulated earlier[4] explains the prevailing chirality.

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Supplementary Material Available: Tables giving calculated bond lengths and angles for 7–13 and related compounds (22 pages). Ordering information is given on any current masthead page.

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Mercuration of a Ruthenocene. Synthesis, Characterization, and Halogenation of $[(C_5(HgO_2CCH_3)_5)(C_5(CH_3)_5)Ru]$

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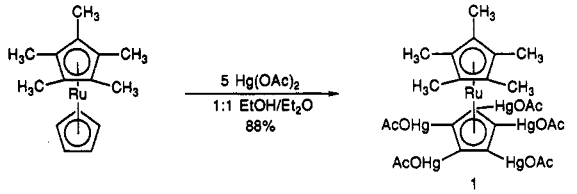
Summary: Treatment of pentamethylruthenocene with 5 equiv of mercuric acetate affords pentakis(acetoxymecurio)pentamethylruthenocene (88%), which can be halogenated with potassium triiodide or potassium tribromide to afford pentaiodopentamethylruthenocene (60%) and pentabromopentamethylruthenocene (35%). The crystal structure of the pentaiodopentamethylruthenocene derivative is described.

Substantial effort has been directed toward both the synthesis of mercurated cyclopentadienyl complexes and their subsequent transformation to functionalized species.[1] Unfortunately, the oxidizing nature of the mercuration process often destroys electron-rich organometallic fragments, so useful chemistry has really only been developed for ferrocene and substituted derivatives. While the mercuration of ruthenocene was reported in a 1960 publication,[2] subsequent work has shown that the interaction of ruthenocene with mercury(II) salts produces ruthenium–mercury-bonded adducts, rather than carbon–mercury bonds.[3] Herein we report that pentamethylruthenocene is preferentially pentamercurated at the unsubstituted cyclopentadienyl ring upon treatment with mercuric acetate in ethanol/diethyl ether. This represents the first well-characterized mercuration of a ruthenocene derivative and suggests that permercuration, rather than monomercuration, may be a general process in metallocene chemistry. Furthermore, the pentamercurated ruthenocene yields the pentahalo derivatives upon treatment with potassium triiodide or potassium tribromide. The crystal structure of pentaiodopentamethylruthenocene is reported and constitutes the first structural evaluation of a complex bearing an η^5-pentaiodocyclopentadienyl ligand.

Treatment of pentamethylruthenocene with mercuric acetate (5 equiv) in 1:1 ethanol/diethyl ether at ambient temperature for 18 h afforded a white precipitate of pentakis(acetoxymecurio)pentamethylruthenocene (1), which was obtained as an analytically pure powder in 88% yield after filtration and vacuum drying (eq 1).[4] The structure of 1 was established by ^1H NMR, infrared spectroscopy, and microanalysis and from reactivity studies (vide infra). In particular, the ^1H NMR spectrum showed no cyclopentadienyl C–H resonances, which indicated that 1 was fully pentamercurated. An experiment was performed in which pentamethylruthenocene was reacted with 1 equiv of mercuric acetate in 1:1 ethanol/diethyl ether for 18 h. Workup afforded 1 (18%) and recovered pentamethylruthenocene (78%). This indicates that the rates of mercuration for the intermediate mercurated species are all faster than the initial mercuration of pentamethylruthenocene.



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(1)

The ^1H NMR spectrum of 1 was complicated. At ambient temperature in dichloromethane-d_2, four singlets (δ 2.07, 1.98 (br), 1.95 (br), 1.92) were observed. Upon cooling of the sample to −80 °C, seven resonances were obtained (δ 2.02, 1.97, 1.93, 1.90, 1.88, 1.80, 1.72). The 60 °C spectrum in benzene–d_6 showed two equal intensity singlets at δ 2.22 and 2.12. We propose that this behavior arises from acetate isomerism that occurs when the oxygen or methyl is either pointed up toward the Cp* ring or away from it. At low temperature, this would result in a sta-

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[1] For leading references, see: Fung, C. W.; Roberts, R. M. G. *Tetrahedron* **1980**, 3289. Floris, B.; Illuminati, G. *Coord. Chem. Rev.* **1975**, *16*, 107. Kitching, W. *Organomet. Chem. Rev.* **1968**, *3*, 35. Makarova, L. G. In *Organometallic Reactions*; Becker, E. I., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1970; Vol 1, p 119. Popov, V. I.; Lieb, M.; Haas, A. *Ukr. Khim. Zh.* **1990**, *56*, 1115. See also: Amiet, G.; Nicholas, K.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1970**, 161. Nesmeyanov, A. N.; Anisimov, K. N.; Valuava, Z. P. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1962**, 1683. Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

[2] Rausch, M. D.; Fischer, E. O.; Grubert, H. *J. Am. Chem. Soc.* **1960**, *82*, 76.

[3] Nesmeyanov, A. N.; Lubovich, A. A.; Gubin, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 1823. Morrison, W. H.; Hendrickson, D. H. *Inorg. Chem.* **1972**, *11*, 2912. Gusev, A. I.; Struchkov, U. T. *Zh. Strukt. Khim.* **1972**, *6*, 1121. Genisovich, L. I.; Zakurin, N. V.; Bezrukova, A. A.; Gubin, S. P. *J. Organomet. Chem.* **1974**, *81*, 207.

[4] Preparation of 1: A 250-mL round-bottomed flask was charged with pentamethylruthenocene (0.904 g, 3.00 mmol), mercuric acetate (4.78 g, 15.0 mmol), ethanol (100 mL), diethyl ether (50 mL), and a stir bar and was fitted with a rubber septum. The solution was stirred at ambient temperature for 18 h, during which time an off-white solid precipitated. The precipitate was collected on a medium glass frit and was washed succesively with ethanol (20 mL), ether (20 mL), and hexane (20 mL). Vacuum drying afforded 1 as an analytically pure off-white powder (4.19 g, 88%): decomposition range, with evolution of elemental mercury, 230–250 °C; IR (KBr) ν_{CO} 1570 (vs); ^1H NMR (CD_2Cl_2, 23 °C, δ) 2.07 (s), 1.98 (s, broad), 1.95 (s, broad), 1.92 (s). Anal. Calcd for $C_{25}H_{30}Hg_5O_{10}Ru$: C, 18.83; H, 1.90. Found: C, 18.84; H, 1.93.

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