

Preliminary communication

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Ruthenium(0) Catalyzed Isomerization  
of Allylbenzene. The Detection and  
Isolation of A Hydrido- $\eta^3$ -Allyl Intermediate

Edward O. Sherman, Jr.<sup>+</sup> and Merle Olson  
Department of Chemistry, University of Western Ontario,  
London, Ontario (Canada)

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SUMMARY

Allylbenzene is isomerized to cis- and trans- $\beta$ -methylstyrene at 35-60°C in the presence of  $[(C_6H_5)_3P]_4Ru(\pi-CH_3CN) \cdot CH_3CN$ . Two hydrido- $\eta^3$ -1-phenylallyl ruthenium complexes have been detected by proton nmr spectroscopy during the reaction and the predominant one of formula  $[(C_6H_5)_3P]_2RuH(\eta^3-C_3H_4C_6H_5)(CH_3CN)$  has been isolated. The structure of this intermediate contains cis phosphines, mutually trans hydrido and acetonitrile ligands and the 1-phenylallyl ligand in a syn-configuration. A similar structure with an anti-configuration of the 1-phenylallyl ligand is suggested for the other detected intermediate. These complexes indicate that this isomerization is initiated by oxidative-addition of ruthenium(0) to an allylic C-H bond with the formation of distinct  $\eta^3$ -allyl metal hydride species as has been proposed in a number of metal catalyzed olefin transformations.

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<sup>+</sup> Present address: Department of Chemistry, Eastern Illinois University,  
Charleston, Illinois, 61920

One of the mechanisms currently accepted for the transition metal catalyzed isomerization of olefins involves an intramolecular 1,3-hydrogen shift. Although the essential  $\eta^3$ -allyl-hydride exchange step of this mechanism has been directly observed [1], it has not been possible to detect the intermediates during the limited number of isomerizations which proceed by this mechanism [2, 3]. Thus, it has not been established whether a hydrido- $\eta^3$ -allyl complex, as originally proposed [4], is formed during the isomerization or whether the reaction occurs in a concerted fashion [3]. We wish to report that hydrido- $\eta^3$ -allyl complexes can be readily detected by  $^1\text{H}$  nmr spectroscopy during the isomerization of allylbenzene catalyzed by  $(\pi\text{-acetonitrile})\text{tetrakis}(\text{triphenylphosphine})\text{ruthenium}(0)$ . Furthermore, one of the intermediates has been isolated and fully characterized by analysis and spectroscopic measurements.

Cole-Hamilton and Wilkinson [5] have recently reported the synthesis of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ru}(\text{H})[\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2](\text{CH}_3\text{CN})$  by sodium amalgam reduction of  $[(\text{C}_6\text{H}_5)_3\text{P}]_n\text{RuCl}_2$  ( $n = 3$  or  $4$ ) in 10%  $\text{CH}_3\text{CN}$ /tetrahydrofuran solvent. On the basis of a similarity in melting point, certain features in the infra-red spectrum and reactivity with propene these authors suggest that the ortho-metallated complex is identical to the compound,  $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Ru}(\pi\text{-CH}_3\text{CN})\cdot\text{CH}_3\text{CN}$ , which was prepared by electrochemical reduction in acetonitrile [6]. The following data for the electrosynthesized complex, however, proves that this material is a different compound which is not ortho-metallated: (1) no upfield resonance attributable to a hydride ligand is detected in the  $^1\text{H}$  nmr spectrum; (2) peaks at  $1550$  and  $1410\text{ cm}^{-1}$  characteristic of an ortho-metallated phenyl ring are absent in the infra-red spectrum; (3) elemental analysis [7] is in accord with the empirical formula  $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Ru}(\text{CH}_3\text{CN})_2$ ; (4) synthesis [6] of the analogous complex,  $[(2,6\text{-D}_2\text{C}_6\text{H}_3)_3\text{P}]_4\text{Ru}(\text{CH}_3\text{CN})_2$ , has no effect on the position or intensity of the infra-red peak at  $1910\text{ cm}^{-1}$   $[\nu(\pi\text{-CN})]$  which is fortuitously identical to  $\nu(\text{RuH})$  in the ortho-metallated complex. Thus, the original formulation of the electrosynthesized compound is believed to be correct and is used throughout this paper. The isolation of these two distinct compounds by apparently similar reactions is tentatively attributed to the

different solvent systems employed rather than the method of reduction. In acetonitrile solvent the formation of a coordinatively unsaturated ruthenium(0) complex, as proposed by Cole-Hamilton and Wilkinson [5], would be suppressed by solvent coordination thereby making the ortho-metallation reaction unfavorable. The formation of a coordinatively unsaturated ruthenium(0) intermediate presumably also plays a key role in the reaction of  $[(C_6H_5)_3P]_2Ru(H)[C_6H_4P(C_6H_5)_2](CH_3CN)$  with propene to yield  $[(C_6H_5)_3P]_2Ru(H)(\eta^3-C_3H_5)(CH_3CN)$ .

In acetonitrile solution under nitrogen allylbenzene is quantitatively isomerized to cis- and trans- $\beta$ -methylstyrene (yield, 98%) at 60°C in the presence of  $[(C_6H_5)_3P]_4Ru(\pi-CH_3CN) \cdot CH_3CN$ . At this temperature the reaction is complete in 2-5 hours for olefin to catalyst molar ratios of 7.5:1 and 81:1, respectively. The ratio of cis- to trans- $\beta$ -methylstyrene, determined chromatographically, is 5:95 which is in good agreement with the expected thermodynamic ratio [8]. Upon completion of the reaction the initial ruthenium(0) complex was recovered unchanged from the reaction mixture and was identified by its infra-red spectrum and melting point.

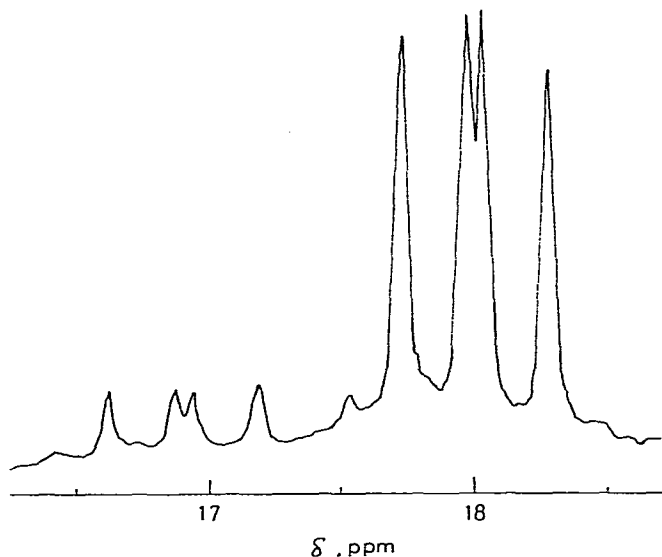


Figure 1. Proton nmr spectrum of metal hydride region during  $[(C_6H_5)_3P]_4Ru(\pi-CH_3CN) \cdot CH_3CN$  catalyzed isomerization of allylbenzene at 60°C in  $CD_3CN$ .

In an attempt to detect the catalytic intermediate during the isomerization, the reaction was carried out in a nmr tube in acetonitrile- $d_3$  at  $60^\circ\text{C}$  and an allylbenzene to catalyst ratio of 7.5:1. The spectrum obtained 30 minutes after the reaction was initiated exhibited downfield signals due to both  $\beta$ -methylstyrene [1.88 (d), 6.30 (m) ppm] and allylbenzene [3.25 (d), 4.9 (m), 5.0 (m), 5.8 (m) ppm]. The relative intensities of the resonances of allylbenzene and  $\beta$ -methylstyrene indicated that at this time the isomerization was 75% complete. Two upfield resonances (Figure 1) characteristic of ruthenium hydrido species were also observed at 16.9 and 18.0 ppm.

Each hydride signal consists of a doublet of doublets and the phosphorus-hydrogen coupling constants are indicative of cis phosphorus coupling. The ratio of the intensity of the more prominent signal at 18.0 ppm ( $J_{\text{PH}}$ , 24.9 and 30.2 Hz) to that at 16.9 ppm ( $J_{\text{PH}}$ , 25.0 and 31.7 Hz) was 7.8:1. When the reaction mixture was cooled to room temperature a yellow precipitate formed. The infra-red spectrum of this solid showed that it was a mixture of  $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Ru}(\pi\text{-CH}_3\text{CN})\cdot\text{CH}_3\text{CN}$  and a hydrido ruthenium complex which exhibited a characteristic  $\nu(\text{Ru-H})$  band at  $1953\text{ cm}^{-1}$ . The detection of hydrido species both during the isomerization and in the recovered solid product suggested that it might be possible to isolate the intermediate(s) early in the isomerization at a high substrate to catalyst ratio.

Treatment at  $50^\circ\text{C}$  of a stirred slurry of  $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Ru}(\pi\text{-CH}_3\text{CN})\cdot\text{CH}_3\text{CN}$  (0.200g) and allylbenzene (0.0943g) in acetonitrile (10 ml) under nitrogen yields a homogeneous solution within 10 minutes. After 30 minutes the mixture was cooled to  $-5^\circ\text{C}$  whereupon  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{RuH}(\eta^3\text{-C}_3\text{H}_4\text{C}_6\text{H}_5)(\text{CH}_3\text{CN})$  separated as yellow crystals [9] in 80% yield. The room temperature proton nmr spectrum of this complex in  $\text{C}_6\text{D}_6$  exhibited resonances characteristic of hydride, 1-phenylallyl, aceto-

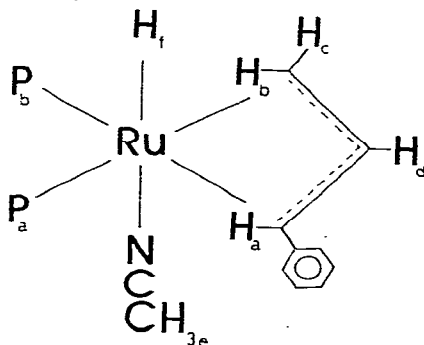


Table 1.  $^1\text{H}$  nmr Data for  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{RuH}(\eta^3\text{-C}_3\text{H}_4\text{C}_6\text{H}_5)(\text{CH}_3\text{CN})$  in  $\text{C}_6\text{D}_6$ 

| nucleus      | $\delta$ , ppm | relative intensity | Coupling constants, Hz                                                                                 |
|--------------|----------------|--------------------|--------------------------------------------------------------------------------------------------------|
| $\text{H}_a$ | 3.09 (dd)      | 1                  | $J_{\text{H}_a\text{H}_d}$ , 9.6; $J_{\text{P}_a\text{H}_a}$ , 5.8                                     |
| $\text{H}_b$ | 1.77 (dd)      | 1                  | $J_{\text{H}_b\text{H}_d}$ , 10.6; $J_{\text{P}_a\text{H}_b}$ , 4.5                                    |
| $\text{H}_c$ | 2.75 (ddd)     | 1                  | $J_{\text{H}_c\text{H}_d}$ , 6.4; $J_{\text{H}_c\text{H}_f}$ , 2.5; $J_{\text{P}_b\text{H}_c}$ , 6.4   |
| $\text{H}_d$ | 6.29 (m)       | 1                  |                                                                                                        |
| $\text{H}_e$ | 0.63 (s)       | 3                  |                                                                                                        |
| $\text{H}_f$ | -17.3 (dd)     |                    | $J_{\text{P}_a\text{H}_f}$ , 25.1; $J_{\text{P}_b\text{H}_f}$ , 20.7; $J_{\text{H}_c\text{H}_f}$ , 2.5 |
| phenyl-H     | 7.1 (m)        | 33                 |                                                                                                        |

nitrile and triphenylphosphine ligands and is consistent with a complex of structure

The chemical shifts, coupling constants and spectral assignments are listed in Table 1. The assignments of the allyl protons given in Table 1 were confirmed by homonuclear decoupling. The  $^{31}\text{P}$  proton decoupled spectrum at  $30^\circ\text{C}$  exhibits two doublets at 58.28 and 65.78 ppm ( $J_{\text{PP}}$ , 14.2 Hz) downfield from an 85%  $\text{H}_3\text{PO}_4$  external reference.

The structure of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{RuH}(\eta^3\text{-C}_3\text{H}_4\text{C}_6\text{H}_5)(\text{CH}_3\text{CN})$  and the marked similarity in chemical shift and splitting pattern observed for the hydride resonance in this compound and those detected during the isomerization of allylbenzene in acetonitrile strongly suggest that the isolated complex is an intermediate in this reaction. Furthermore, these results indicate that the isomerization of allylbenzene with the ruthenium(0) complex proceeds via an intramolecular 1,3-hydrogen shift and that in this system a distinct  $\eta^3$ -allylhydride as suggested by Emerson and Pettit [4] is formed. The isomerization of allylbenzene via a 1,3-hydrogen shift in the presence of ruthenium(0) is to be contrasted with the 1,2-addition-elimination mechanism observed for this substrate with

tetracarbonylhydridocobalt(I) [10] and emphasizes the importance of the metal system on the mechanism of catalysis. The high yield of  $[(C_6H_5)_3P]RuH(\eta^3-C_3H_4C_6H_5)(CH_3CN)$  leads us to assign the structure of this complex to the predominant intermediate detected during isomerization. Based on the observed cis phosphorus coupling, the other intermediate is believed to have a similar structure with the 1-phenylallyl ligand in an anti-configuration. Reductive-elimination from the syn- and anti-isomers would lead to trans- and cis- $\beta$ -methylstyrene, respectively. The observed ratio of syn- to anti-isomers during the isomerization is approximately equal to that of the measured ratio of cis- to trans- $\beta$ -methylstyrene.

The oxidative-addition of  $[(C_6H_5)_3P]_4Ru(\pi-CH_3CN) \cdot CH_3CN$  to simple allylic hydrocarbons yields isolable hydrido- $\eta^3$ -allyl complexes of the type,  $[(C_6H_5)_3P]_2RuH(\eta^3-R)(CH_3CN)$  where R is allyl or methallyl [11]. The structure of these complexes, however, was not determined because of their low solubility and stability in solution. The identical formulation of these compounds with  $[(C_6H_5)_3P]_2RuH(\eta^3-C_3H_4C_6H_5)(CH_3CN)$  suggests that their structures are similar.

The ability to monitor the structure and time-dependent behavior of reactants, products and intermediates during the isomerization of allylbenzene by nmr spectroscopy provides an excellent opportunity to study the kinetics and mechanism of this reaction. Preliminary results indicate that in benzene [12] at 35°C (allylbenzene:catalyst = 9.1:1) the reaction exhibits first-order kinetics ( $k = 4.4 \times 10^{-4} s^{-1}$ ) over approximately five half-lives. The hydrido- $\pi$ -allyl intermediates are formed rapidly ( $\leq 10$  minutes) and only slowly decrease during the course of the reaction. This behavior suggests that the oxidative-addition of ruthenium to an allylic bond of allylbenzene is faster than a subsequent rate determining step in the reaction which leads to the formation of  $\beta$ -methylstyrene.

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## References and Notes

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- 7 Anal. Calcd. for  $[(C_6H_5)_3P]_2RuH[C_6H_4P(C_6H_5)_2]CH_3CN$ : C, 72.40; H, 5.21; P, 10.00; N, 1.50. Calcd. for  $[(C_6H_5)_3P]_4Ru(CH_3CN)_2$ : C, 74.07; H, 5.40; P, 10.05; N, 2.27. Found: C, 74.2; H, 5.30; P, 10.0; N, 2.20.
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- 9 Anal. Calcd. for  $[(C_6H_5)_3P]_2Ru(C_3H_5C_6H_5)(CH_3CN)$ : C, 71.91; H, 5.52; P, 7.89. Found: C, 71.40; H, 5.33; P, 8.11. Infra-red spectrum (Nujol mull): 2259  $[\nu(CN)]$ ; 1956  $[\nu(RuH)]$ ; 1308  $[\delta(CH_2)]$ ; 999  $[\delta(C-C)]$ ; 903  $[\delta(CH)]$ ; 558  $[\delta(CCC)]cm^{-1}$ . m. p. 188° (d).
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- 12 It should be noted that the isomerization of allylbenzene is much faster in benzene than in a coordinating solvent such as acetonitrile.