# Catalytic Double Bond Isomerization by Polystyrene-Anchored $RuCl_2(PPh_3)_3$

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Dichlorotris(triphenylphosphine)ruthenium has been anchored to diphenylphosphinated styrene-divinylbenzene copolymer. The resulting leaching-resistant catalyst was employed successfully for the isomerization of allylbenzenes and allyl alcohols in numerous turnovers. The stability of the catalyst was examined in different media, and its performances were compared with those of homogeneous  $RuCl_2(PPh_3)_3$  and with those of polymer-bound as well as of free  $RhCl(PPh_3)_3$  and  $IrCl(CO)(PPh_3)_2$ .

The anchoring of soluble transition-metal complexes to insoluble supports has been the subject of considerable research in recent years.<sup>1</sup> Immobilized catalysts with rather good performances and high selectivities for hydrogenation, hydrosilylation, carbonylation, hydroformylation, oligomerization, and some other reactions have been developed. Yet, we noticed that, so far, the heterogenized catalysts have hardly been utilized in "international" izomerization of olefins (cf. ref 1a).

Since in recent years almost all the "classical" homogeneous catalysts have already been immobilized, it is remarkable that no satisfactory supported version of the versatile  $RuCl_2(PPh_3)_3$  has been reported.<sup>1</sup> Attempts to attach this complex for effecting H-D exchange in ethanol and for hydrogenation of olefins met with only partial  $success.^2$ 

We now report the anchoring of  $RuCl_2(PPh_3)_3$  to a polystyrene matrix and demonstrate its application in double bond migration in allylarenes  $(eq 1)^3$  and in the transformation of alkyl(and aryl)vinylcarbinols into ketones (eq 2).<sup>4</sup>

$$ArCH_{2}CH = CH_{2} \rightarrow 1$$

$$l cis-ArCH = CHCH_{3} + trans-ArCH = CHCH_{3} (1)$$

$$2$$

$$\begin{array}{c} \operatorname{RCH}(\operatorname{OH})\operatorname{CH}=\operatorname{CH}_2 \to \operatorname{RCOCH}_2\operatorname{CH}_3 \\ 4 & 5 \end{array}$$
(2)

#### **Results and Discussion**

By application of the general procedure for introduction of homogeneous catalysts [such as RhCl(PPh<sub>3</sub>)<sub>3</sub><sup>5</sup> or IRCl(CO)(PPh<sub>3</sub>)<sub>2</sub><sup>6</sup>] onto phosphinated crosslinked polystyrene, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> was incorporated into a polystyryldiphenylphosphine resin (eq 3). The resulting MINGIN

polymer-bound ruthenium catalyst promoted reaction 1 and could be reused in hundreds of catalytic cycles with only exceedingly small loss of catalytic activity (vide infra). In fact, the activity proved to increase during the few initial runs until maximum effectiveness has been reached. A similar increase in catalytic power after the first run has already been noted in olefin hydrogenation by some polymer-bound rhodium complexes.<sup>7,8</sup>

In a typical experiment, in which a mixture of 0.13 g (1.1) mmol) of allylbenzene (1, Ar =  $C_6H_5$ ), 85 mg (1.1 × 10<sup>-2</sup> mequiv of Ru) of catalyst 7a, 1.4 mL of mesitylene, and 0.1 mL of 1-methylnaphthalene was heated under argon at 140 °C for 90 min, 18% of the substrate isomerized. When the catalyst was filtered and reused in further runs, the conversion of 1 (Ar =  $C_6H_5$ ) increased to 50%, 80%, and 87% in the second, third, and fourth cycle, respectively.

The activities of the analogous supported RhCl(PPh<sub>3</sub>)<sub>3</sub> (7b) and  $IrCl(CO)(PPh_3)_2$  (7c) complexes were similar to that of 7a in the first run. However, neither 7b nor 7c became more active in consecutive turnovers. The rhodium catalyst lost as much as two-thirds of its activity upon being recycled during the first three runs due to extensive leaching processes.

The isomerization of 4-allylanisole  $(1, Ar = 4-CH_3OC_6H_4)$ by 7a-c proved to proceed similarly. Some typical conversion turnover profiles are shown in Figure 1.

Comparison of the isomerization rates of 1 (Ar =  $C_6H_5$ , 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) by the anchored catalysts 7a-c with those obtained with the aid of their soluble counterparts (Table I) indicates that the catalyst strength is reduced by a factor of 2-5.5 upon heterogenizing. However, as the activity of the homogeneous catalyst is often lost upon recycling un-

<sup>(1)</sup> Some recent reviews: (a) Hartley, F. R.; Vezey, P. N. Adv. Organomet. Chem. 1977, 15, 189; (b) Manecke, G.; Stork, W. Angew. Chem., Int. Ed. Engl. 1978, 17, 657; (c) Leznoff, C. C. Acc. Chem. Res. 1978, 11, 328; (d) Pittman, C. U.; Hirao, Q. N. A.; Honnick, W.; Hanes, R. In "Relations between Homogeneous and Heterogeneous Catalysis"; CNRS: Paris, 1978; pp 49-94; (e) Scurrel, M. S. Catalysis (London) 1978, 2, 215 - 42

 <sup>(2)</sup> Strathdee, G. Z.; Given, R. Can. J. Chem. 1974, 52, 3000.
 (3) For RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>-catalyzed isomerization of allylarenes under homogeneous conditions see: Blum, J.; Pickholtz, Y. Isr. J. Chem. 1969, 7, 723

<sup>(4)</sup> For RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>-catalyzed conversion of alkylvinylcarbinols into ethyl alkyl ketones see: Sasson, Y.; Rempel, G. L. Tetrahedon Lett. 1974, 4133.

<sup>(5)</sup> Grubbs, R. H.; Kroll, L. C. J. Am. Chem. Soc. 1971, 93, 3062.
(6) Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. J. Am. Chem. Soc. 1972, 94, 1789.

<sup>(7)</sup> Brzezinska, Z. C.; Cullen, W. R.; Strukul, G., private communication.

<sup>(8)</sup> Strukul, G.; Dolimpio, P.; Bonivents, M.; Pina, P.; Graziani, M. J. Mol. Catal. 1976, 2, 179.



Figure 1. Conversion-turnover profiles for the isomerization of all vlanisole by supported ruthenium  $(\bullet)$ , rhodium (O), and iridium ( $\blacktriangle$ ) catalysts 7a-c under comparable conditions. Each run was performed at 140 °C for 90 min under 99.9% argon with 236 mg (1.6 mmol) of substrate,  $1.6 \times 10^{-2}$  mequiv of catalyst, 1.9 mL of mesitylene, and 0.1 mL of 1-methylnaphthalene.

Table I. Maximum Rates<sup>a</sup> of Allylarene Isomerization by Homogeneous and by Heterogenized Ru, Rh, and Ir Catalysts under Comparable Conditions<sup>b</sup>

	10 <sup>3</sup> (max rate of conversion), <sup>c</sup> mmol L <sup>-1</sup> min <sup>-1</sup>	
catalyst	$1, Ar = C_{\mathfrak{s}}H_{\mathfrak{s}}$	1, $Ar = 4$ - $CH_3OC_6H_4$
RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	21.7	22.7
7a 7	8.7	10.3
RhCl(PPh,),	16.7	18.0
7b	2.9	3.5
IrCl(CO)(PPh <sub>2</sub> ) <sub>2</sub>	5.1	5.8
7c	1.1	1.3

<sup>a</sup> The maximum rates of the homogeneous systems and of 7b and 7c are identical with the initial rates. The figures for 7a-catalyzed isomerization correspond to initial rates in advanced cycles. <sup>b</sup> Conditions as in Figure 1. <sup>c</sup> Since the isomerization by the heterogenized catalysts is assumed to take place within the pores of the beads rather than on their surfaces, the reaction rates of both the homogeneous and the heterogeneous systems have the same units.

der our conditions and the immobilized complexes can be reused in further runs, the heterogeneous system can be regarded as the more efficient one. The ruthenium catalyst 7a became particularly efficient after 3-5 turnovers. This increase in effectiveness of the catalyst was associated with color change of the beads from purple to yellow-orange. In terms of the suggestion of Strathdee and Given<sup>2</sup> that divalent ruthenium is partially oxidized upon heterogenization and in light of the recent finding that homogeneous ruthenium catalysts form isolable ruthenium hydride species during allylbenzene isomerization,<sup>9</sup> we considered the possibility that these *chemical* modifications<sup>10</sup> may be responsible for the gradual color change of the catalyst. While we could not find any evidence for the existence of an anchored Ru(III) species, we observed the formation of a sharp Ru-H IR band (KBr) at 2060 cm<sup>-1</sup> during the activation period of 7a. The Ru-H peak disappeared on prolonged exposure of the activated beads to air or upon quenching with various electrophiles. (The air-oxidized catalyst showed a characteristic absorption at 880 cm<sup>-1</sup>.) Thus, we conclude that the rate acceleration during the first few cycles results from slow formation of immobilized



Figure 2. Isomerization of 4-allylanisole by 7a in pure mesitylene (O) and in mesitylene-benzyl alcohol (17:3) (•). Each run was carried out at 140 °C for 35 min (under Ar) in 2 mL of solvent with 1.6 mmol of substrate and  $1.6 \times 10^{-2}$  mequiv of 7a (prepared for the first run from 15.3 mg of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and 92 mg of phosphinated polystyrene).

ruthenium hydride. Further support of this assumption had been provided both by experiments in which external hydrogen donors (e.g., 15% w/w benzyl alcohol or 1phenylethanol)<sup>11</sup> were added and by reactions carried out under an H<sub>2</sub> atmosphere. In these experiments the reaction rate reached maximum value, the Ru-H IR peak grew to maximum intensity, and complete color change of the beads took place during the *first* catalytic cycle. When deuterated carbinols (e.g.,  $C_6H_5CD(CH_3)OD$ ) were employed, the 2060-cm<sup>-1</sup> band did not appear. In the absence of a potent hydrogen donor the formation of metal hydride may be rationalized by ortho metalation<sup>12</sup> or by slow hydrogen abstraction from the solvent or substrate.<sup>13</sup>

As the formation of a metal hydride may be associated with extrusion of hydrogen chloride from the chlorinecontaining catalyst (cf., ref 14) that may by itself promote double bond migration in olefins,<sup>15</sup> we conducted control experiments in the presence of 2,6-di-tert-butylpyridine. The absence of any detectable effect of the hindered base excludes acid-catalyzed isomerization in our system.

As shown for some other polymer-attached catalysts,<sup>1</sup> the activity of 7a was solvent dependent (cf., however, ref 16). Aromatic hydrocarbons of good swelling capacity of 2% crosslinked polystyrene lead to higher rates than, e.g., aliphatic hydrocarbons, alcohols, or ethers. Thus, under the conditions of Figure 1 the relative initial rates of 4allylanisole isomerization in (a) mesitylene, (b) 1methylnaphthalene, (c) decaline, (d) n-decane, and (e) diethylene glycol diethyl ether were in the fourth run: 1.00, 0.83, 0.62, 0.46, and 0.47, respectively. It should be noted. however, that the order was different in the *first* catalytic run (prior to catalyst activation) in which the rate in the ether was 2.5 times faster than that in mesitylene.

Mixtures of good swelling solvents and potent hydrogen donors promoted catalyst efficiency. For example, the isomerization of 4-allylanisole by 7a in mesitylene-benzyl alcohol (17:3) is compared with the reaction in pure mesitylene in Figure 2.

The effect of the solvent on the activity of the catalyst proved to be reversible. Thus, when the medium was

- (11) Sasson, Y.; Blum, J. J. Org. Chem. 1975, 40, 1887.
  (12) See, e.g.: Parshall, G. W. Acc. Chem. Res. 1970, 3, 139.
  (13) D'Aniello, M. J., Jr.; Barefield, E. K. J. Am. Chem. Soc. 1978, 100, 1474.
  - (14) Moseley, K.; Maitlis, P. M. J. Chem. Soc. A 1970, 2884
  - (15) See, e.g.: Hubert, A. J.; Reiminger, H. Synthesis, 1970, 405.
     (16) Holy, N. L. J. Org. Chem. 1979, 44, 239.



Figure 3. Isomerization of allylbenzene by 7a in mesitylene  $(\bullet)$ , n-decane (I), and mesitylene-benzyl alcohol (17:3) (O). Each run was carried out under an Ar atmosphere for 90 min at 140 °C with 141 mg (1.2 mmol) of substrate and  $1.2 \times 10^{-2}$  mequiv of catalyst (prepared from 11.5 mg of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and 69 mg of phosphinated polystyrene).



Figure 4. Concentration-time profiles for the reactant and products in catalytic isomerization of 4-allylanisole (1, Ar =  $CH_3OC_6H_4$ ; 1.6 mmol) by 7a (fourth turnover; 1.6 × 10<sup>-2</sup> mequiv) in 2 mL of mesitylene at 140 °C under argon: O, 4-allylanisole; ■, cis-1-(4-methoxyphenyl)prop-1-ene; ●, trans-1-(4-methoxyphenyl)prop-1-ene.

changed after several turnovers to a better or a worse solvent, the rate and conversion changed accordingly. If, thereafter, the orginal solvent was reused, the system resumed its original properties (see Figure 3).

Typical reaction composition curves for 7a-catalyzed isomerization of allylanisole at 140 °C at maximum catalyst activity are shown in Figure 4. Under these conditions an equilibrium mixture that was obtained after 90 min consisted of 90.0% of trans- and 8.9% of cis-1-(4-methoxyphenyl)prop-1-ene and of 1.1% of starting material. Except for the first catalytic run, the reaction had no detectable induction period and proved to follow first-order kinetics in the substrates having a linear log C vs. time relationship for a large range of experimental conditions.

Reaction 1 (Ar = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) was studied at various temperatures between 112 and 152 °C (substrate concentration 0.5-1.5 M) by using supported catalysts. From plots of log  $C_0/C$  vs. time such as shown in Figure 5, the reaction constants could be derived, and the activation energy was found to be  $9.8 \pm 0.5$  kcal mol<sup>-1</sup>.

Under homogeneous conditions (i.e., in the presence of  $RuCl_2(PPh_3)_3$ ) the isomerization of 4-allylanisole in mesitylene (Figure 6) followed first-order kinetics at low substrate concentrations (<0.32 M). The activation energy of this system was shown to be  $22.4 \pm 0.5$  kcal mol<sup>-1</sup>. The difference in the observed  $E_a$  values for homogeneous and heterogeneous catalysis suggests that the latter reaction is diffusion controlled. The ratio  $E_s(\text{homo})/E_s(\text{hetero}) =$ 2.26 is in good agreement with the prediction<sup>17</sup> that ob-



**Figure 5.** Plots of log  $C/C_0$  against time for reaction 1 (Ar =  $4-CH_3OC_6H_4$ ) at various temperatures with fully activated 7a as catalyst: initial substrate concentration 0.8 M in 2 mL of mesitylene,  $1.6 \times 10^{-2}$  mequiv of catalyst, temperature range 112–152 °C.



Figure 6. Concentration-time profiles for the reactants and products in catalytic isomerization of 4-allylanisole (1, Ar =  $CH_3OC_6H_4$ ; 1.44 mmol) by  $RuCl_2(PPh_3)_3$  (1.44 × 10<sup>-2</sup> mmol) in 1.8 mL of mesitylene: reaction temperature 140 °C, Ar atmosphere.

served activation energies of reactions that are influenced by strong pore resistance are equal to half of the true activation energies. It should be noted that although  $E_{a}$ (hetero) <  $E_{a}$ (homo) the rate of the homogeneous catalysis was faster than that of the heterogeneous reaction, owing to the compensation effect of the preexponential factor in the Arrhenius equation. By extrapolation of the frequency factors in the corresponding Arrhenius plots, it was found that A(homo) = 22.5 and  $A(\text{hetero}) = 4.8^{18}$  As the frequency factor is exponentially proportional to  $\Delta S^*$ the smaller value of A(hetero) reflects on the loss of freedom associated with catalyst fixation in the polymer matrix.<sup>19</sup>

In contrast to some silica-bound metal catalysts<sup>20</sup> the activity of 7a was not increased by effective stirring. This suggests that in our system the diffusion factors that affect the rate arise from the resistance inside the catalyst channels rather than from the concentration gradient around the surface of the beads. This difference between silica- and polystyrene-supported catalysts can be ration-

<sup>(17)</sup> See, e.g.: Levenspiel, O. "Chemical Reaction Engineering", 2nd ed.; Wiley: New York, 1972; p 491.

<sup>(18)</sup> By assuming the catalytic process by 7a to take place in the spheres of the polymeric catalyst rather than on its surface, one finds that the units of k (hetero) become the same as those of k (homo). Thus direct comparison of A(hetero) and A(homo) is permissible.
 (19) Terasama, M.; Kaneda, K.; Imanaka, T.; Teraniski, S. J. Catal.

<sup>1978, 51, 406.</sup> 

<sup>(20)</sup> Conau, J.; Bartholin, M.; Guyot, A. J. Mol. Catal. 1975, 1, 375.

Table II. Rates of Isomerization of Substituted Allylbenzenes by Free and by Supported  $\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{3}$  at 140 °C<sup>a</sup>

	10 <sup>3</sup> (rate at 20% conver- sion), mmol L <sup>-1</sup> min <sup>-1</sup>		
starting compd	supported catalyst <sup>b</sup>	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	
C,H,CH,CH=CH,	3.0	21.7	
4-CIC, H, CH, CH=CH,	4.2	25.0	
$4 - CH_{C}H_{A}CH_{C}H_{C}H_{C}H_{C}H_{C}H_{C}H_{C}H_{$	2.9	23.2	
$4-CH_{3}OC_{6}H_{4}CH_{2}CH=CH_{2}$	3.2	22.7	
3,4-OCH <sub>2</sub> OC <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	2.3	11.5	

<sup>a</sup> Initial substrate concentration 0.8 M (in 2 mL of mesitylene); ruthenium content  $1.6 \times 10^{-2}$  meauiv. <sup>b</sup> In contrast to Table I, the rates correspond to the *first* catalytic cycle.

Table III. Trans/Cis Ratios of Products in 7a- and in RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>-Catalyzed Isomerization of Allylbenzenes under Comparable Conditions<sup>a</sup>

	ratio of <i>trans</i> - to <i>cis</i> -1-arylprop-1-ene	
starting compd	heterogeneous catalysis	homogeneous catalysis
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	2.0	7.1
4-CIC, H <sub>4</sub> CH, CH=CH,	2.2	8.0
$4-CH_3C_6H_4CH_2CH=CH_2$	2.1	7.3
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	2.5	6.6

<sup>a</sup> At 30% conversion. Reaction conditions: 1.6 mmol of substrate and  $1.6 \times 10^{-2}$  mequiv of catalyst in 2 mL of mesitylene at 140 °C.

alized in light of the mode of anchoring of the active species. While in silica catalysts the metal is attached to the large outer surface of the support, the active sites in 7a lay mostly inside the beads (which have relatively small surfaces).<sup>21</sup> In this context it is noteworthy that under our conditions the isomerization of allylbenzene by beads of small diameter (<0.2 mm) proceeded at a slightly higher rate than by those with 0.2–0.6-mm diameters.

Rates of isomerization of some substituted allylbenzene by  $RuCl_2(PPh_3)_3$  and by 7a under comparable conditions are given in Table II. The figures indicate that like in the RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>-catalyzed transformation of 1,4-diarylbutenes<sup>22</sup> both the homogeneous and the heterogeneous isomerizations of allylbenzenes are virtually independent of the electronic nature of the substrate. However, the product distribution differs considerably in the two catalyst systems prior to equilibration. While the allylbenzenes shown in Table II were transformed by 7a (fourth run) into the corresponding trans- and cis-1-arylprop-1-enes in a ratio of 2.1-2.5 at 30% conversion (Table III), the catalysis by RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (preheated for 15 h at 130 °C in mesitylene) led to a trans-cis ratio of 6.6-8.0. Similar enhanced formation of the cis isomers has already been noticed in some other isomerization reactions by immobilized catalysts.<sup>23</sup> As the reaction profiles clearly indicate that up to 50% conversion the cis-1-arylprop-1-enes results from the allylbenzenes rather than from the kinetically less favorite trans compounds, it may be concluded that this selectivity is associated with the structural requirements of the polymeric catalyst.

Table IV. Maximum Rates<sup>a</sup> of Rearrangement of Allyl Alcohols RCH(OH)CH=CH<sub>2</sub> by Supported Catalysts 7a-c and by Their Homogeneous Counterparts<sup>b</sup>

	10 <sup>2</sup> (max rate of conversion), <sup>a</sup> mmol L <sup>-1</sup> min <sup>-1</sup>		
catalyst	$R = CH_3 - (CH_2)_4$	$R = CH \\ (CH_2)$	$\begin{array}{c} I_3 \cdot R = \\ {}_6 C_6 H_5 \end{array}$
$\frac{\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{3}}{\operatorname{7a}}$ RhCl(PPh_{3})_{3} 7b IrCl(CO)(PPh_{3})_{2}} 7c	9.0 2.6 6.2 2.2 2.1 0.46	$     \begin{array}{r}       10.5 \\       2 2 \\       6.7 \\       1.7 \\       2.3 \\       0.36 \\     \end{array} $	8.7 2.1 6.0 1.7 1.7 0.40

<sup>a</sup> See footnote a of Table I. <sup>b</sup> Reaction conditions: initial substrate concentration 0.8 M in 2 mL of mesitylene; amount of catalyst  $1.6 \times 10^{-2}$  mequiv; 140 °C under argon.



Figure 7. Conversion-turnover profiles for 7a-catalyzed rearrangement of 1-decen-3-ol. Each run was performed with the same sample of catalyst (ruthenium content  $1.6 \times 10^{-2}$  mequiv) and 250 mg (1.6 mmol) of substrate in 2.0 mL of mesitylene under 99.9% pure argon at 140 °C for 35 min.

Data on the rearrangement of some allyl alcohols by 7a-c and by their homogeneous counterparts are listed in Table IV. As for the previous system, the soluble catalysts led to higher initial rates than the heterogenized ones but suffered from two disadvantages: (a) they promoted some allyl alcohol disproportionation<sup>5,24</sup> (eq 4) along with the

$$2RCH(OH)CH=CH_{2} \rightarrow RCOCH=CH_{2} + RCH(OH)CH_{2}CH_{3} (4)$$

isomerization reaction (eq 2); (b) they often deteriorated in the presence of the unsaturated carbinols to give insoluble and inactive aggregates and metallic depositions. The supported catalysts promoted exclusively reaction 2 and could be recycled successfully for many consecutive runs.

A conversion-turnover profile for 7a-catalyzed rearrangement of 1-decen-3-ol in mesitylene is shown in Figure 7. As for the allylbenzenes, the activity of the catalyst increased during the first four cycles, but the changes in rate were more moderate and finally became slightly negative after the fifth run. This comparative catalyst deactivation is attributed to metal leaching induced by the hydroxyl-containing substrate. It is remarkable that although metal elution can be observed in *most* of the current supported catalysts, it has very often been disregarded, and the factors responsible for the phenomenon are mentioned only in a few papers (see, e.g., ref 25 and 26).

<sup>(21)</sup> Arai, H. J. Catal. 1978, 51, 134.

<sup>(22)</sup> J. Blum and Y. Becker, J. Chem. Soc., Perkin Trans. 2 1972, 982. (23) E.g.: Sbrama, G.; Braca, G.; Valentini, G.; Pazienza, G.; Altomare, A. J. Mol. Catal. 1977, 3, 111.

 <sup>(24)</sup> Sasson, Y.; Rempel, G. L. Can. J. Chem. 1974, 52, 3825.
 (25) Allum, K. G.; Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, P. J. J. Catal. 1976, 43, 322.

### Polystyrene-Anchored RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>

Table V. Degree of Ruthenium Elution from Supported RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (7a) during 90 Min at 140 °C under Various Conditions<sup>a</sup>

reactant	medium	min ruthenium content of catalyst after 90 min, %
none	n-decane	100
none	decaline	100
none	mesitylene	100
none	1-methylnaphthalene	100
none	diethylene glycol diethyl ether	99.40
4-allylanisole	mesitylene	99.82
4-allylanisole	mesitylene, ambient atmos- phere	96.40
4-allylanisole	85% mesitylene, 15% ben- zyl alcohol	99.25
4-allylanisole	mesitylene, triphenylphos- phine <sup>b</sup>	97.70
4-allylanisole	mesitylene, triphenyl- amine <sup>b</sup>	99.82
4-allylanisole	diethylene glycol diethyl ether	98.90
1-decen-3-ol	mesitylene	99.25

<sup>a</sup> If not otherwise stated, under argon atmosphere.

<sup>b</sup> Molar ratio of additive/catalyst of 3:1.

With the aid of atomic emission spectroscopy<sup>27</sup> we have shown that immobilized  $RuCl_2(PPh_3)_3$ , 7a, is by far more leaching resistant than the analogous rhodium and iridium catalysts 7b and 7c. Under our standard reaction conditions for 4-allylanisole isomerization (1.6 mmol of substrate,  $1.6 \times 10^{-2}$  mequiv of catalyst, 2.0 mL of mesitylene, 90 min at 140 °C under argon), the relative amount of eluted metal from 7a-c in the first catalytic cycle proved to be 1.0, 3.0, and 1.5, respectively. As in other cases<sup>28</sup> the soluble extract had no catalytic activity. Therefore, it is understandable that the high rate of leaching from 7b leads to significant loss of catalytic power after the first turnover (see Figure 1).

Under exclusion of air and in the absence of substrate no leaching from 7a could be detected even after the mixture had been subjected to prolonged heating at 140 °C in oxygen-free hydrocarbons (see Table V). However, in polar solvents leaching became quite significant. The addition of allylbenzene that can compete with the phosphinated polymer on a coordination site proved to induce up to 0.15% metal extrusion into mesitylene during the first 90 min at 140 °C. In consecutive runs the degree of leaching decreased and became insignificantly small. When the allylbenzene was substituted by the oxygencontaining allylanisole, the loss of supported metal in the first run increased up to 0.18%. Addition of moderate quantities of benzyl alcohol to the reaction mixture has been shown above to enhance the catalytic process (Figure 2). However, the hydroxyl-containing additive increased metal extrusion as well (up to 0.75% per cycle under the conditions of Table V). A similar rate of leaching was recorded also during the catalytic rearrangement of 1-decen-3-ol (Table V). The highest degree of metal extraction was observed when the catalyses were conducted under ambient atmosphere. Substitution of argon by air in allylanisole isomerization caused a 20-fold increase in leaching, viz., loss of half of the original ruthenium content of 7a during 14 catalytic cycles. Whether this extensive metal elution is associated with partial destructive cleavage of the ruthenium hydride intermediate<sup>29</sup> or with some oxidation of the polymer-bound phosphine ligands<sup>30</sup> is yet uncertain.

Added phosphines have an unusual effect on catalyses 1 and 2 by 7a. Both trialkyl- and triarylphosphines (not tertiary amines) caused extensive leaching but yielded soluble species that were themselves very active isomerization catalysts. Thus, the rate of 4-allylanisole isomerization by 7a at 140 °C increases by 20%, 120%, and 200%, respectively, upon addition of 3 mol of  $(4-ClC_6H_4)_3P$  $(C_6H_5)_3P$ , and  $(4-CH_3C_6H_4)_3P$  per equivalent of supported ruthenium. Under these conditions approximately 70% of the catalytic activity can be attributed to the eluted metal. This observation stands in contrast to the findings that free triphenylphosphine inhibits hydrogenation and hydrosilvlation reactions catalyzed by heterogenized rhodium and platinum-phosphine complexes.<sup>20,31</sup> We have shown that contrary to the effect of phosphines on  $RhCl(PPh_3)_3$ - and  $IrCl(CO)(PPh_3)_2$ -promoted isomerization of allylbenzene,<sup>4</sup> they serve as potent cocatalysts for the eluted ruthenium species.

Although 7a in mesitylene is leaching resistant both at 112 and at 152 °C, the loss of metal is usually temperature and solvent dependent in the presence of substrate. During allylanisole isomerization in mesitylene the ruthenium elution increases by a factor of 1.5 on raising the temperature from 112 to 152 °C. In diethylene glycol diethyl ether, elution increases by a factor of 3.5 when the temperature is changed from 140 to 160 °C.

## **Experimental Section**

Allylbenzene, 4-allylanisole, 1-allyl-3,4-methylenedioxybenzene, 1-octen-3-ol, and 1-decen-3-ol were purchased from Fluka AG, Buchs (highest grade). Prior to use they were subjected to column chromatography over neutral alumina, distilled, and degassed. 3-Phenylprop-1-en-3-ol,<sup>32</sup> 4-chloroallylbenzene,<sup>33</sup> and 4-allyltoluene<sup>34</sup> were prepared as described and purified as above. The phosphines  $[(4-ClC_6H_4)_3P, (4-CH_3C_6H_4)_3P]$ , complexes  $[RuCl_2-$ (PPh<sub>3</sub>)<sub>8</sub>, RhCl(PPh<sub>3</sub>)<sub>3</sub>, IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>], and phosphinated supports [2% crosslinked and 20% crosslinked polymer-bound triphenylphosphine on styrene-divinylbenzene copolymer (beads 20-60 mesh)] were purchased from Strem Chemical Co. The complexes and phosphines were recrystallized and analyzed prior to use. All solvents were AR grade and were dried over CaH<sub>2</sub> at least 24 h, distilled under argon, and degassed.

Anchoring Catalysts to Diphenylphosphinated Polystyrene Resins. Catalysts 7b and 7c were prepared by phosphine-ligand exchange according to the literature.<sup>5</sup> Polymerbound RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (7a) was prepared by the following procedure. A mixture of 1.34 g of 2% crosslinked polymer-bound triphenylphosphine on styrene-divinylbenzene copolymer (0.62 mequiv of P), 197 mg of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.2 mequiv of Ru), and 10 mL of dry benzene was refluxed under argon for 6 days. The solvent was decanted, and the residue was extracted six times with 20 mL of hot benzene (until the extract was free of ruthenium). The purple beads were dried at 80 °C in vacuo and stored under 99.9% pure argon. The combined benzene solutions were evaporated, and the ruthenium content of the residue was determined by atomic emission techniques with a Perkin-Elmer 403 instrument with an acetylene-nitrous oxide flame at 372 nm. Methyl isobutyl ketone was used as the solvent.<sup>27</sup> The phosphorus contents of both the extract and the resin were determined by

(31) Michalska, Z. M. J. Mol. Catal. 1977, 3, 125.
 (32) Duveen, D. I.; Kenyon, J. J. Chem. Soc. 1939, 1697.

(33) Frisch, K. C. J. Polym. Sci. 1959, 41, 359.

<sup>(26)</sup> Lang, W. H.; Juremicz, A. T.; Haag, W. O.; Whitehurst, D. D.; Rollmann, L. D. J. Organomet. Chem. 1977, 134, 85.

<sup>(27)</sup> Braca, G.; Cioni, R.; Sbrana, G.; Scandiffio, G. At. Absorpt. Newsl. 1975, 14, 39.

<sup>(28)</sup> Blond, P.; Rio, A.; Cordier, G.; Edelga, G.; Sangonard, Y. J. Mol. Catal. 1978, 4, 181.

<sup>(29)</sup> Sherman, E. O., Jr.; Olson, M. J. Organomet. Chem. 1979, 172, C13.

<sup>(30)</sup> E.g.: Lyons, J. E. J. Chem. Soc. D 1971, 562.

<sup>(34)</sup> Hurd, C. D.; Bollman, H. T. J. Am. Chem. Soc. 1934, 56, 1447.

the usual molybdenum blue method.<sup>35</sup>

Isomerization of 4-Allylanisole with Polymer-Bound  $\operatorname{RuCl}_2(\operatorname{PPh}_3)_3$  (7a). In a typical experiment, a 20-mL Schlenk tube equipped with a neoprene seal was purged with 99.9% pure argon and charged with 107 mg of 7a  $(1.6 \times 10^{-2} \text{ mequiv of Ru})$ . The reaction vessel was cooled to 0 °C, and into it there was injected a solution of 236 mg (1.6 mmol) of 4-allylanisole in 1.9 mL of mesitylene and 0.1 mL of 1-methylnaphthalene (internal standard). The tube was immersed at once into an oil bath regulated at 140  $\pm$  0.2 °C. Samples  $(1-2 \ \mu L)$  were withdrawn periodically from the mixture and immediately frozen at -78 °C. GLC analysis was performed on a 6.32  $\times$  2000 mm copper column packed with 20% DC 200 on 80-100-mesh Chromosorb P at 150 °C. After 90 min the liquid was decanted off (under argon), and the solid beads were washed three times with 10 mL of degassed benzene, dried under argon at 70 °C for 15 h, and then carried

(35) Chalmers, R. A.; Thomson, D. A. Anal. Chim. Acta 1958, 18, 575.

through an identical reaction procedure again.

Similar procedures were applied for the isomerization of the other allylic compounds by the three supported catalysts.

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**Registry No.** 1 (Ar =  $C_{6}H_{5}$ ), 300-57-2; 1 (Ar =  $4-CH_{3}OC_{6}H_{4}$ ), 140-67-0; 1 (Ar =  $4-ClC_{6}H_{4}$ ), 1745-18-2; 1 (Ar =  $CH_{3}C_{6}H_{4}$ ), 3333-13-9; 1 (Ar =  $3,4-OCH_{2}OC_{6}H_{3}$ ), 94-59-7; 2 (Ar =  $C_{6}H_{5}$ ), 766-90-5; 2 (Ar =  $4-ClC_{6}H_{4}$ ), 1879-52-3; 2 (Ar =  $4-CH_{3}C_{6}H_{4}$ ), 2077-29-4; 2 (Ar =  $4-CH_{3}OC_{6}H_{4}$ ), 25679-28-1; 3 (Ar =  $C_{6}H_{5}$ ), 873-66-5; 3 (Ar =  $4-ClC_{6}H_{4}$ ), 1879-53-4; 3 (Ar =  $4-CH_{3}C_{6}H_{4}$ ), 2077-30-7; 3 (Ar =  $4-CH_{3}OC_{6}H_{4}$ ), 1879-53-4; 3 (Ar =  $4-CH_{3}C_{6}H_{4}$ ), 2077-30-7; 3 (Ar =  $4-CH_{3}OC_{6}H_{4}$ ), 180-23-8; 4 (R =  $CH_{3}(CH_{2})_{4}$ ), 3391-86-4; 4 (R =  $CH_{3}(CH_{2})_{6}$ ), 928-80-3; RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, 15529-49-4; RhCl(PPh<sub>3</sub>)<sub>3</sub>, 14694-95-2; IrCl(CO)-(PPh<sub>3</sub>)<sub>2</sub>, 15318-31-7.

# Kinetic Properties of Caged Ambident Radicals Formed in the Thermolyses of Nitrones<sup>1,2</sup>

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Thermal decompositions of N-benzhydryl- $\alpha,\alpha$ -diphenylnitrone (1) and the para-tetradeuterated analogue 1- $d_4$  in several solvents are reported. Mass spectral analyses of recovered nitrones and/or O-benzhydryl ethers were performed. These data are combined with previously reported spectroscopic rate constants for the decomposition of 1 to evaluate the true carbon-nitrogen homolysis rate constant and the relative rate constants for (a) geminate radical recombination at the iminoxy nitrogen, (b) irreversible recombination at oxygen, and (c) diffusion of the solvent-caged radicals.

### Introduction

The thermal decomposition of N-benzhydryl- $\alpha,\alpha$ -diarylnitrones in several different solvents involves the homolysis of a carbon-nitrogen bond forming iminoxy and benzhydryl radicals.<sup>3</sup> The lifetime of the initially formed caged radical pair is limited primarily by the occurrence of three competitive processes, namely, recombination at nitrogen to regenerate nitrone, irreversible recombination at oxygen to form O-benzhydryloxime, and diffusion from the cage.<sup>4</sup> The present study describes experiments which provide a measure of the true homolysis rate constant and of relative rates of destruction of the caged radical pair via the three paths mentioned above.

An understanding of the kinetic properties of these caged radical pairs can be derived from measurements of isotopic compositions of products formed from the thermal decompositions of mixtures of N-benzhydryl- $\alpha$ , $\alpha$ -diphenylnitrone (1) and its tetra-p-deuterated analogue 1- $d_4$ .

#### Results

The synthesis of  $1-d_4$  has been recently described.<sup>45</sup> For the crossover experiments, mixtures of the deuterated and

(5) The samples employed in these studies were comprised of 81.3 tetra, 17.56% tri, and 1.11% dideuterated species.

undeuterated nitrones 1 and  $1-d_4$  were decomposed in degassed solutions prepared from either diethylcarbitol (diethylene glycol diethyl ether), *tert*-butyl alcohol, or N,N-dimethylacetamide. In one run the mixture of nitrones was decomposed as a melt at 173 °C. The products were separated chromatographically and the isotopic composition of the O-benzhydryloxime and/or the recovered nitrone was then determined mass spectroscopically.<sup>6</sup> Control experiments (employing mass spectral analyses) with nitrones and O-ethers of known isotopic composition demonstrated that neither isotopic scrambing nor structural isomerization occurred during the isolation and separations following partial or total decompositions of nitrone mixtures. Table I summarizes the product analyses for decompositions of mixtures of 1 and 1-d<sub>4</sub>.

The degree of intramolecularity,  $\alpha$ , was determined by comparing the mole fraction of dideuterated species (m/e365) found in the O-ether or nitrone with that expected from a purely statistical recombination of benzhydryl and iminoxy radicals. The degree of intramolecularity is defined in eq 1, where  $X_{365}$  is the mole fraction of di-

$$\alpha = (X_{365} - D_{365}) / (C_{365} - D_{365}) \tag{1}$$

deuterated species in the isolated nitrone or O-ether,  $D_{385}$ is the mole fraction of dideuterated species which would be formed from a completely statistical recombination of radicals, and  $C_{385}$  is the mole fraction of dideuterated species in the starting mixture of nitrones 1 and 1- $d_4$ . The general methods and discussion of approximations for

<sup>(1)</sup> Abstracted from the Thesis of J. A. Villarreal, University of California, San Diego, and San Diego State University. A preliminary report of this study has been published.<sup>2</sup>

<sup>(2)</sup> Villarreal, J. A.; Grubbs, E. J. J. Am. Chem. Soc. 1974, 96, 7594.
(3) See: (a) Villarreal, J. A.; Dobashi, T. S.; Grubbs, E. J. J. Org. Chem. 1978, 43 1890; (b) Grubbs, E. J.; Villarreal, J. A.; McCullough, J. D., Jr.; Vincent, J. S. J. Am. Chem. Soc. 1967, 89, 2234; (c) Vincent, J. S.; Grubbs, E. J. Ibid. 1969, 91, 2022; (d) Dobashi, T. S.; Parker, D. R.; Grubbs, E. J. Ibid. 1977, 99, 5382; Morris, D. G. J. Chem. Soc. D 1971, 221.

 <sup>(4)</sup> Villarreal, J. A.; Grubbs, E. J. J. Org. Chem. 1978, 43, 1896.
 (5) The samples employed in these studies were comprised of 81.33%

<sup>(6)</sup> The isotopic compositions of isolated tetraphenylethane samples were not determined. Neither was any attempt made to isolate benzophenone oxime from the decomposition products.