Communications to the Editor

The First Isolated, Stable *cis*-Hydridoalkylrhodium Complexes and Their Reductive Elimination Reaction

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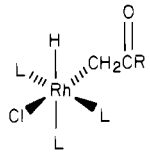
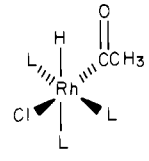
cis-Hydridoalkylrhodium complexes have been postulated as intermediates in a number of useful organic processes homogeneously catalyzed by rhodium complexes such as olefin hydrogenation and aldehyde decarbonylation.[1] Recently an unstable intermediate hydridoalkylrhodium complex has been intercepted and characterized spectroscopically at −78 °C in a catalytic hydrogenation reaction.[2] Such rhodium complexes, however, have not been isolated so far. We report here the first isolation of pure, fully characterized, and relatively stable *cis*-hydridoalkylrhodium complexes from a homogeneously catalyzed epoxide isomerization reaction and the direct observation of their reductive elimination. Our evidence suggests that this rarely observed[2-4] but important alkyl-hydride reductive elimination process of a transition-metal complex proceeds by a dissociative mechanism.

We have recently found that (trimethylphosphine)iridium(I) complexes react with epoxides to afford *cis*-hydridoacylmethyliridium(III) complexes. Catalytic transformation of the epoxides in these reactions does not take place since these iridium(III) complexes are remarkably stable and do not undergo alkyl-hydride reductive elimination even under forcing conditions.[5] Extending our studies to (trimethylphosphine)rhodium complexes, we have observed that upon reaction of $Rh(PMe_3)_3Cl$[6] (**1**) with epoxides, catalytic isomerization of the epoxides to ketones takes place at ambient conditions, and the Rh(I) complex is quantitatively converted into a *cis*-hydridoalkylrhodium(III) complex that can be easily isolated.

Stirring an orange solution[7] of **1** in propylene oxide at 25 °C under N_2 for 16 h and submitting the resulting yellow solution to high-vacuum distillation result in a yellow solid. Recrystallization of the solid from toluene/pentane at −50 °C yields the analytically pure complex **2** (L = PMe_3) as white needles in 82%



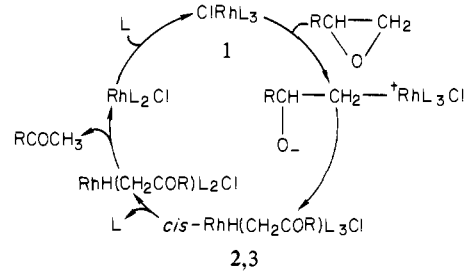


2, R = Me
3, R = Ph

4

yield.[8] GC and NMR analysis of the distillate reveals formation of 700% (based on Rh) of acetone. Since the ^1H NMR and ^{31}P NMR spectra of **2** are consistent only with a structure containing a trimethylphosphine ligand trans to the hydride ligand and having two identical trans trimethylphosphine ligands, the hydrido and alkyl ligands have to be in mutually cis positions, as shown in structure **2**.

Scheme I[a]



2,3

[a] L = PMe_3.

Table I. Observed Rate Constants for the Reductive Elimination of *cis*-$HRh(CH_2COCH_3)(PMe_3)_3Cl$ (**2**) in the Presence of Added PMe_3 and at Various Temperatures[a]

temp, °C	$[PMe_3]$, M	$10^5 k_{obsd}$, s^{-1}
31	0	9.48
31	0.263	6.25
31	0.557	5.62
31	0.869	4.22
31	1.500	2.62
27	0	5.69
35	0	18.42
44	0	55.46

[a] Concentration of **2** = 5×10^{-2} M.

Styrene oxide reacts with **1** in a similar fashion, yielding the complex **3**[9] and acetophenone in 60% and 1200% yields, respectively. Much higher yields of acetone and acetophenone are obtained at higher temperatures (e.g., 85 cycles to acetone at 70 °C).

Reaction of **1** with ethylene oxide gives rise to complex **4** in 75% yield in addition to acetaldehyde (400%) instead of the expected formylmethyl complex **5**. The latter is probably formed initially but reductively eliminates acetaldehyde, which then readds to give complex **4** (eq 1).[10]

$$\underset{\mathbf{5}}{cis\text{-}RhH(CH_2CHO)(PMe_3)_3Cl} \rightarrow CH_3CHO + \underset{\mathbf{1}}{Rh(PMe_3)_3Cl} \rightarrow \mathbf{4} \quad (1)$$

Complexes **2** and **3** undergo slow reductive elimination under ambient conditions, yielding acetone and acetophenone, respec-

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(2) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.
(3) Intramolecular hydridoalkyl reductive elimination has been observed with *cis*-$PtH(R)(PR_3)_2$: Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.
(4) *cis*-$OsH(CH_3)(CO)_4$ undergoes intermolecular reductive elimination: Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 295.
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(6) Jones, R. A.; Mayor Real, F.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511.
(7) All operations were carried out in a N_2 drybox with dry, degassed solvents. Reactions with ethylene oxide were performed in sealed vessels.
(8) **2**: IR (Nujol) 1650 (s, $\nu_{C=O}$), 1940 (s, ν_{Rh-H}); ^1H NMR (C_6D_6) δ 2.13 (s, 3 H, CH_3CO), 1.48 (d of t of d, J_{H-P_1} = 7.0 Hz, J_{H-P_2} = 6.9 Hz, J_{H-Rh} = 3.4 Hz, 2 H, $RhCH_2$), 1.39 (t, J_{H-P} = 3.2 Hz, 18 H, 2 PMe_3), 0.85 (d of d, J_{H-P} = 6.2 Hz, J_{H-Rh} = 0.7 Hz, 9 H, PMe_3), −9.70 (d of d of t, $J_{H-P,trans}$ = 207.4 Hz, $J_{H-P,cis}$ = 17.0 Hz, J_{H-Rh} = 11.6 Hz, 1 H, RhH); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −6.29 (d of d, J_{P-Rh} = 102.2 Hz, J_{P-P} = 29.4 Hz, 2 P), −24.79 (d of t, J_{P-Rh} = 81.4 Hz, J_{P-P} = 29.3 Hz, 1 P); ^{31}P NMR (C_6D_6) δ −6.29 (d of d of d, J_{P-Rh} = 102.2 Hz, J_{P-P} = 29.4 Hz, $J_{P-H,cis}$ = 17.0 Hz), −24.79 (d of d of t, $J_{P-H,trans}$ = 207.4 Hz, J_{P-Rh} = 81.4 Hz, J_{P-P} = 29.3 Hz).
(9) **3**: IR (Nujol) 1625 (s, $\nu_{C=O}$), 1955 cm^{-1} (s, ν_{Ir-H}); ^1H NMR (C_6D_6) δ 0.99 (d of d, J_{H-P} = 6.6 Hz, J_{H-Rh} = 1.0 Hz, 9 H, PMe_3), 1.31 (t, J_{H-P} = 3.2 Hz, 18 H, PMe_3), 2.00 (d of t of d, J_{H-P_1} = 6.6 Hz, J_{H-P_2} = 7.2 Hz, J_{H-Rh} = 3.2 Hz, 2 H, $RhCH_2$), −9.54 (d of d of t, $J_{H-P,trans}$ = 209.3 Hz, $J_{H-P,cis}$ = 16.4 Hz, J_{H-Rh} = 10.0 Hz, 1 H, RhH), 7.01-7.18 (m, 3 H, Ph), 7.70-7.82 (m, 2 H, Ph).
(10) **4** can be obtained directly by oxidative addition of acetaldehyde to **1**: Milstein, D., submitted for publication.

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tively, and regenerating the starting Rh(I) complex **1** (eq 2), thus

$$cis\text{-}RhH(CH_2COR)(PMe_3)_3Cl \rightarrow RhCl(PMe_3)_3 + CH_3COR \quad (2)$$

completing the catalytic cycle for the epoxide isomerization reaction. Isolation of the complexes **2** and **3** as the major Rh species in the catalytic reaction undoubtedly points out that the overall reductive elimination process **2**,**3** → **1** is rate determining in the catalytic cycle. Since this process proceeds by a prior slow PMe_3 dissociation from **2** (vide infra), this phosphine dissociation step is rate determining in the catalytic isomerization process. The mechanism of epoxide isomerization catalyzed by **1** is thus plausibly presented by Scheme I.

Kinetic measurements of the reductive elimination process of **2** were carried out by monitoring the concentration of **2** as well as that of the products, $ClRh(PMe_3)_3$ (**1**) and acetone by ^1H NMR and ^{31}P NMR in C_6D_6 between 27 and 44 °C. First-order plots for the disappearance of **2** are invariably linear for at least 3 half-lives and are unaffected by variations in the initial concentration of **2**. Activation parameters obtained from a linear Arrhenius plot of k_{obsd} are (31 °C) as follows: E_a = 25.6 kcal/mol, $\Delta H^{\ddagger}$ = 25.0 kcal/mol, $\Delta G^{\ddagger}$ = 23.4 kcal/mol, $\Delta S^{\ddagger}$ = 5.3 eu. In the presence of added PMe_3, the reaction rate is inhibited and the stoichiometry is altered to that of eq 3.[11] Still, disappearance

$$cis\text{-}RhH(CH_2COCH_3)(PMe_3)_3Cl + PMe_3 \rightarrow CH_3COCH_3 + \underset{\mathbf{6}}{[Rh(PMe_3)_4]^+Cl^-} \quad (3)$$

of **2** obeys first-order kinetics (Table I), and the reciprocal of k_{obsd} varies linearly with the concentration of added PMe_3. Also, in the presence of the "Phosphine sponge" $Rh(acac)(C_2H_4)_2$, a 15-fold increase in the rate of **2** disappearance is observed at 27 °C.

The reductive elimination reaction of **2** is *intramolecular*: decomposition of a toluene solution containing equimolar amounts of **2** and the *cis*-deuterioalkyl complex *mer*-$RhD(CD_2COCD_3)(PMe_3)_3Cl$ (**7**) (5×10^{-2} M each), obtained from reaction of **1** with hexadeuteriopropylene oxide, yielded a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 and no crossover products. Kinetic measurements of the rate of decomposition of **7** at 31 °C yield a small kinetic isotope effect k^H_{obsd}/k^D_{obsd} = 1.3.

The above evidence suggests that the reductive elimination of **2** occurs by a dissociative mechanism involving a rate-determining prior loss of PMe_3, as outlined in eq 4-7. Reaction 5 is practically

$$cis\text{-}RhH(CH_2COCH_3)(PMe_3)_3Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RhH(CH_2COCH_3)(PMe_3)_2Cl + PMe_3 \quad (4)$$

$$RhH(CH_2COCH_3)(PMe_3)_2Cl \xrightarrow{k_2} Rh(PMe_3)_2Cl + CH_3COCH_3 \quad (5)$$

$$RhCl(PMe_3)_2 + PMe_3 \overset{fast}{\rightleftharpoons} RhCl(PMe_3)_3 \quad (6)$$

$$RhCl(PMe_3)_3 + PMe_3 \xrightarrow{fast} [Rh(PMe_3)_4]^+Cl^- \quad (7)$$

irreversible; no reaction between acetone and **1** takes place at 31 °C, even over periods of weeks.

By employment of the steady-state approximation, the reductive elimination from **2** gives rate law 8. From the intercept of a linear

$$-\frac{d[\mathbf{2}]}{dt} = \frac{k_1k_2[\mathbf{2}]}{k_{-1}[PMe_3] + k_2} = k_{obsd}[\mathbf{2}] \quad (8)$$

plot of $1/k_{obsd}$ vs. $[PMe_3]$ follows $k_1 = 1.02 \times 10^{-4}$ s^{-1}, corresponding to an activation-free energy $\Delta G^{\ddagger}$ (31 °C) = 23.3 kcal/mol. This indicates that the PMe_3 ligands are very tightly bound to the Rh(III). For comparison, the rate constant for PPh_3 dissociation from *mer*-$RhH_2(PPh_3)_3Cl$ at 30 °C is approximately 4×10^2 s^{-1}.[12] The ratio k_{-1}/k_2 = 1.83 is obtained from the slope of this plot, indicating that the rate of the reductive elimination step (5) is comparable to that of the reassociation process.

Our studies demonstrate for the first time a requirement for ligand dissociation prior to intramolecular hydridoalkyl reductive elimination; the rate of reductive elimination from *cis*-$PtH(Me)(PPh_3)_2$ is not affected by added PPh_3.[3] Dialkyl reductive elimination from square-planar Pd[13,14] and Au[15] complexes also takes place by a dissociative mechanism and has been proposed theoretically[16] to proceed from a cis-"T"-shaped intermediate. Similar considerations may be applied to octahedral hydridoalkyl complexes by taking into account only the plane of the reductively eliminating groups.

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Registry No. 1, 36103-64-7; **2**, 82555-23-5; **3**, 82555-24-6; **4**, 82555-25-7; propylene oxide, 75-56-9; styrene oxide, 96-09-3; ethylene oxide, 75-21-8.

(11) The C_6D_6-insoluble cationic complex **3**[6] is undoubtedly formed as a result of fast reaction between **1** and PMe_3; not even traces of **1** could be detected when reaction 3 was monitored by ^{31}P NMR.

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Simplification and Assignment of Carbon-13 Spectra by Using *J*-Resolved NMR Spectroscopy in Solids

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In the high-resolution solid-state ^{13}C NMR called CP/MAS,[1] signal assignment is usually made by referring to the spectrum in solution. However, some substances exhibit characteristic spectra in the solid state, and many others are insoluble in solvents or decompose on melting. Therefore, it is desirable to develop a method that is capable of signal assignment in solids. In a previous paper,[2] we reported that *J* multiplets can be observed under homonuclear decoupling with magic-angle sample spinning (MAS); this method provides an assignment aid in solids. In complex molecules, however, resonance lines in *J* spectra are usually overlapping each other so heavily that complete assignment is hampered. This communication describes a modification that facilitates the assignment of ^{13}C spectra in solids; the resonances always appear as sharp singlets, resulting in time saving.

The pulse sequence that we used for the simplification and assignment of ^{13}C spectra in solids is depicted in Figure 1; it is one of various possible alternatives. In the first τ interval, the homonuclear decoupling to the protons suppresses spin diffusion so that MAS is then able to remove ^{13}C-^1H dipolar and anisotropic *J* coupling but not the isotropic *J* coupling; in the second τ interval, all three of the heteronuclear interactions are removed. The evolution under chemical-shift interactions is refocused by a 180° pulse. Therefore, the ^{13}C magnetization *M* at the commencement of data acquisition depends only on the time evolution in the first τ interval under the isotropic ^{13}C-^1H *J* coupling:

$$M_n(\tau) = M_n(0)\cos^n(\pi SJ\tau) \qquad n = 0\text{-}3 \quad (1)$$

where *S* designates the scaling factor of the used homonuclear decoupling and *n* is the number of protons that are directly bonded

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