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Alkane Dehydrogenation Catalyzed by Rhodium(I) Phosphine Complexes: Observation of the Stoichiometric Alkane-to-Rhodium Hydrogen-Transfer Step

Kuo-Chen Shih and Alan S. Goldman*

*Department of Chemistry, Rutgers, The State University of New Jersey,
New Brunswick, New Jersey 08903*

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Summary: $\mathrm{RhL_2Cl}$ ($\mathrm{L = P^iPr_3}$) is found to dehydrogenate cyclooctane to give $\mathrm{H_2RhL_2Cl}$ and cyclooctene; this represents the first observation of the key hydrogen-transfer step proposed for related, catalytic alkane transfer–dehydrogenation systems. Using norbornene as a hydrogen acceptor, transfer–dehydrogenation is catalyzed but turnover numbers are low.

We and others have recently reported the first efficient homogeneous catalytic systems for the dehydrogenation of alkanes. Initially, $\mathrm{Rh(PMe_3)_2(CO)Cl}$ was found to catalyze photochemical alkane dehydrogenation.[1–3] More recently, we reported that $\mathrm{Rh(PMe_3)_2ClL'}$ ($\mathrm{L' = CO, PMe_3, P^iPr_3}$) or $\mathrm{[Rh(PMe_3)_2Cl]_2}$ catalyzed extremely efficient thermal transfer–dehydrogenation.[4] The latter system requires both sacrificial hydrogen acceptors (olefins) and (surprisingly) hydrogen atmosphere to be operative. We have proposed that the actual dehydrogenation step in both these systems is the thermal (nonphotochemical) reaction of $\mathrm{Rh(PMe_3)_2Cl}$ with alkane (eq 1).[3,4] In the photochemical system, $\mathrm{Rh(PMe_3)_2Cl}$ is formed via photochemical loss of CO, while in the thermal system eqs 2 and 3 represent the proposed route. The requirement of $\mathrm{H_2}$ is disadvantageous since several moles of acceptor is hydrogenated per mole of dehydrogenated product.[4]

$$\mathrm{Rh(PMe_3)_2Cl + alkane = alkene + Rh(PMe_3)_2ClH_2} \qquad (1)$$

$$\mathrm{Rh(PMe_3)_2ClL' + H_2 = Rh(PMe_3)_2ClH_2 + L'} \qquad (2)$$

$$\mathrm{A + Rh(PMe_3)_2ClH_2 = Rh(PMe_3)_2Cl + AH_2} \qquad (3)$$

$$\mathrm{A = sacrificial\ acceptor}$$

While $\mathrm{Rh(PMe_3)_2Cl}$ is isolable only as a dimer, the bulky monomeric analogs $\mathrm{Rh[P(c\text{-}C_6H_{11})_3]_2Cl}$[5] and $\mathrm{Rh(P^iPr_3)_2Cl}$[6] have been synthesized. These appeared to undergo intramolecular dehydrogenation reactions,[7] in accord with the proposed reactivity of $\mathrm{Rh(PMe_3)_2Cl}$, but no reactions of these species with alkanes (or any free hydrocarbons) have been reported. Presumably the much greater (intermolecular) reactivity of $\mathrm{Rh(PMe_3)_2Cl}$ results from steric factors; eq 1 probably involves a very crowded transition state. Herein we report, however, that $\mathrm{RhL_2Cl}$ (**1**; $\mathrm{L = P^iPr_3}$) does react with cyclooctane in analogy with eq 1. To our knowledge, this is the first observation of the simple net transfer of hydrogen from an alkane to a metal complex, uncoupled with other reactions influencing the reaction thermodynamics (such as coordination of the resulting unsaturate[8–10] or subsequent hydrogenation of an acceptor[11]). We also report that in the presence of a hydrogen acceptor (norbornene), **1** catalyzes cyclooctane transfer–dehydrogenation albeit inefficiently, presumably via a cycle in which eq 4 is the key dehydrogenation step.

$$\underset{\mathbf{1}}{\mathrm{RhL_2Cl}} + \mathrm{cyclooctane} \rightarrow \underset{\mathbf{2}}{\mathrm{RhL_2ClH_2}} + \mathrm{cyclooctene} \qquad (4)$$

1 was synthesized as reported by Werner.[6] (Dinitrogen was rigorously excluded to prevent formation of the stable $\mathrm{RhL_2(N_2)Cl}$.[5,12,13]) Heating (90 °C) a cyclooctane solution of **1** (20 mM) under argon for 12 h results in the formation of cyclooctene (6.3 mM) as determined by GC analysis of the volatiles. ^{31}P NMR of the solution reveals the formation of $\mathrm{H_2RhL_2Cl}$ (**2**; 10.6 mM, 53%), identified by comparison with authentic samples.[6,7,14] Removal of solvent and dissolution of the residue in $\mathrm{C_6D_6}$ enables confirmation by ^{1}H NMR of the yield and nature of **2**.

The reaction of **1** with cyclooctane initially proceeds more rapidly than may be inferred from the above

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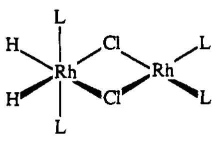
Table I. Thermolysis (90 °C) of RhL_2Cl in Cycloalkanes

solvent	time	$[Rh^0]$	[1]	[2]	[3]	[4]	[5]	[6]	[7]	$[Rh_{tot}]^a$	[L]	$[coe]^b$
cyclooctane	20	19.2	2.4	0.6	1.1	1.1	1.1	1.0	1.3	13.1	3.1	4.5
cyclooctane	180	19.2	0	5.8	0.6	0.9	1.5	0.9	0.8	13.7	2.0	9.5
cyclooctane^c	20	18.6	5.2	0.8	1.5	1.4	0	0.7	0.5	14.2	18.0	5.3
cyclooctane^c	180	18.6	0	9.3	0.4	0.5	0	0.5	0.9	13.9	8.0	14.2
cyclohexane	20	19	9.6	0	0.8	0	0	0.9	0.5	14.0	6.4	
cyclohexane	180	19	0	2.7	0.9	0	3.6	1.9	1.5	14.9	9.6	

^{a} $[Rh_{tot}]$ = [1] + [2] + 2[3] + 2[4] + [5] + 2[6] + 2[7] (concentrations (mM) determined by ^{31}P NMR using a trimethyl phosphate external standard). ^{b} [cyclooctene] determined by addition of CO and subsequent GC analysis of volatiles. ^{c} Added P^iPr_3 (20 mM).

experiments. For example, after 20 min at 90 °C, only 2.4 mM (12%) 1 remains as determined by ^{31}P NMR. A complex mixture of products is observed. These include the following, which are reported or which we have satisfactorily characterized: 2 (0.6 mM); $H_2[RhL_2Cl]_2$[15] (3, 1.1 mM), an analog of the $P(tolyl)_3$ complex reported by Tolman;[16] $H_2Rh_2L_3Cl_2$(cyclooctene)[15] (4, 1.1 mM), an analogue of the PPh_3/*cis*-2-hexene complex reported by Eisenberg;[17] RhL_2Cl_2H[14,18] (5, 1.1 mM). Free L (3.1 mM) is also observed in solution, some of which is accounted for by the formation of 4 and 6 (see below). After 3 h 1 is no longer detectable. The composition of the mixture is shown in Table I. Additionally, ^1H NMR of the residue (C_6D_6) after evaporation of solvent reveals the formation of the paramagnetic complex RhL_2Cl_2,[14] not observable in the ^{31}P NMR spectrum.



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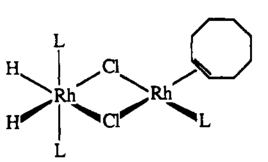

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In addition to the well-characterized products described above, other species are observed to form in the reaction with cyclooctane. Product 6 is tentatively formulated as $\{[(^iPr_2)P(\eta^2\text{-}MeC{=}CH_2)]Rh(\mu\text{-}Cl_2)RhL_2H_2\}$.[15] The ^{31}P NMR spectrum of product 7 is consistent with the presence of two inequivalent Rh(III) centers.[15] Selective decoupling gives a complex pattern which might be attributable to $H_2L_2Rh(\mu\text{-}H_2)RhL_2HCl$.

Addition of CO to the reaction solutions liberates any coordinated cyclooctene formed from the reaction of 1 with cyclooctane ($RhL_2(CO)Cl$ is the major organometallic product). Subsequent trap-to-trap distillation and GC analysis enables precise quantification of the total free and coordinated cyclooctene produced (see Table I).

Heating a cyclohexane solution of 1 affords small quantities of 2. The rate of disappearance of 1 is ca. 3-fold slower than in cyclooctane (48% of 1 remains after 20 min at 90 °C, versus 12% remaining in cyclooctane solutions). In cyclohexane-d_{12} solutions, ^1H NMR and selectively ^1H-decoupled ^{31}P NMR reveal that the hydride product 2 is not deuterated. In a typical run, after 180 min, 2.7 mM 2-h_2 is observed. 3, 5, 6, and 7 are also observed (Table I), and together these products account for 14.9 mM or 75% total rhodium. Only ca. 0.5 mM cyclohexene is observed by GC. When either the cyclooctane or cyclohexane reaction solutions (after 7 h of thermolysis) are exposed to an H_2 atmosphere, conversion to 2 is observed (75 and 58% respectively, after 20 min at ambient temperature).

The above results demonstrate that dehydrogenation of the ligands occurs in cyclohexane solution, while in cyclooctane a competition between ligand and solvent dehydrogenation takes place (the former at ca. half the rate of the latter). The much greater reactivity of cyclooctane, which has been reported in several dehydrogenation systems,[11] presumably results from its significantly lower enthalpy of dehydrogenation (23 vs 28 kcal/mol for cyclohexane). This thermodynamic difference apparently manifests itself in the transition state, which must therefore have some alkene character (reflecting either β-elimination or a subsequent step).

Note that if the failure to observe cyclohexane dehydrogenation were due to the reversibility of the reaction, with the equilibrium favoring the back-reaction, then in the case of C_6D_{12} we would presumably observe H/D scrambling with the hydrides formed by dehydrogenation of the ligand. In fact, no such scrambling is observed. To test for the possibility of H/D exchange with the ligand hydrogens, RhL_2ClD_2 was prepared independently; it was found (^1H NMR) to undergo H/D exchange with the phosphines only very slowly (ca. 7% protiation of the Rh(H/D) position after 9 h at 90 °C).

The presence of excess P^iPr_3 does not inhibit reaction 4. The yields of 2 and cyclooctene are in fact significantly *raised* in the presence of 20 mM L (Table I). This is presumably due to inhibition of the formation of inactive products which contain less than two phosphine ligands per rhodium, including 4 and 6.

Although after 20 min the cyclooctane reaction mixtures show only small amounts of 2, we believe that 2 is both the initial dehydrogenation product and the thermodynamic product at extended reaction times. However, upon its formation in the presence of unreacted 1 and cyclooctene, 2 reacts to form $H_2[RhL_2Cl]_2$ (3) and $H_2Rh_2L_3Cl_2$(cyclooctene) (4). Accordingly, mixing equal volumes of 42 mM solutions of 1 and 2 at 20 °C results in the rapid formation of 3 (15 mM) (the equilibrium constant for this reaction, determined at several concentrations, is 380 ± 40 M^{-1}). When cyclooctene (15 mM) is added to an identical solution, the following distribution of products is observed: 1 (1.1 mM), 2 (2.1 mM), 3 (2.2 mM), 4 (6.6 mM).

When a cyclooctane solution of 1 (10.0 mM) and a good hydrogen acceptor, norbornene (2.0 M), is heated to 90 °C, transfer dehydrogenation is observed as monitored by GC. Plots of formation of cyclooctene and norbornane vs

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[15] Selected NMR data (^{31}P, 81 MHz; ^1H, 400 MHz) are as follows. $H_2[RhL_2Cl]_2$ (3): ^{31}P, δ 56.49 (d, J_{RhP} = 113 Hz), 54.01 (d, J_{RhP} = 194 Hz). $H_2Rh_2L_3Cl_2$(cyclooctene) (4): ^{31}P, δ 56.77 (d, J_{RhP} = 182 Hz), 55.52 (dt, J_{RhP} = 114, J_{PH} = 14.9 Hz); ^1H, δ −21.85 (m, J_{RhH} = 24.0, J_{PH} = 15.2, J_{HH} = 12.0 Hz), −22.58 (m, J_{RhH} = 24.1, J_{PH} = 15.0, J_{HH} = 12.0 Hz). $\{[(^iPr_2)P(\eta^2\text{-}MeC{=}CH_2)]Rh(\mu\text{-}Cl_2)RhL_2H_2\}$ (6): ^{31}P, δ 58.36 (d, J_{RhP} = 181 Hz), 55.67 (dt, J_{RhP} = 114, J_{PH} = 15.0 Hz). $L_2Rh(\mu\text{-}H_2)RhL_2HCl$ (7): ^{31}P, δ 56.19 (d, J_{RhP} = 114 Hz), 55.92 (dt, J_{RhP} = 113Hz).

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time are approximately linear for ca. 5 h, at which point the concentration of each product is ca. 11 mM. The reaction slows down considerably after ca. 10 h and is essentially over after 55 h; the concentrations of cyclooctene and norbornane are then 41 and 37 mM, respectively. The initial rate of catalysis is not diminished by the presence of 30 mM free L; indeed the cyclooctene and norbornane concentrations reached 11 mM after only 3 h. The reaction did not proceed significantly further, however, and the final product concentrations (22 h) were only ca. 14 mM. Interpretation of these results awaits further study. Cyclohexane is not catalytically dehydrogenated under the above conditions (<0.5 mM cyclohexene is formed) in accord with its failure to react with 1 in the absence of a hydrogen acceptor.

In summary, RhL_2Cl effects both the stoichiometric and catalytic dehydrogenation of cyclooctane. These results support the proposed role of $Rh(PMe_3)_2Cl$ as the alkane-dehydrogenating intermediate in thermal and photochemical catalytic systems described previously. Unlike the PMe_3 systems, the present system requires neither light nor H_2 to generate the active three-coordinate species. The catalytic effectiveness of the complex, however, is severely limited by dehydrogenation of the P^iPr_3 ligand. Attempts are underway to characterize the ligand reactions and to design more robust ligands accordingly.

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