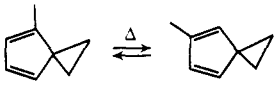

8 **9**

Vapor state pyrolysis of either **8** or **9** in a static system at 513–543°K provides an equilibrium mixture of **8** (~60%) and **9** (~40%). The pyrolyses are remarkably clean; no volatile products other than **8** or **9** are detectable by GLPC analysis, and >98% of the starting material is recovered as the spiroheptadienes **8** and **9**. Kinetic analysis provides $E_a = 44$ kcal/mol, $\Delta S^{\ddagger} = +2 \pm 1.5$ eu. The greater stability of **8** (approximately 0.4 kcal/mol under these conditions) may originate, at least in part, from the unusual electronic structure proposed for this spirodiene ring system.[1] Calculations by the MINDO/1 method[9] predict the standard heat of formation of **8** to be approximately 0.9 kcal/mol lower than that of **9** in qualitative agreement with the observed result.

The mechanisms of thermal [1,5]-alkyl shifts in cyclopentadienes have been extensively investigated for a number of systems,[2,10–15] and a rather delicate energy balance between the concerted and radical pathways is frequently apparent. The activation energy of 44 kcal/mol for the interconversion of **8** and **9** is in good agreement with that reported for pyrolysis of **1**,[2] and the positive activation entropy is suggestive of the intervention of the diradical. The estimated activation energy of 50–56 kcal/mol for homolysis of the 1,5,5-trimethylcyclopentadienes[15] corrected for the difference in cleavage of a secondary C–C bond (compare: D_{C-C} (C_2H_6) = 88 kcal/mol and D_{C-C} (C_3H_8) = 85 kcal/mol)[16] provides an estimate of 47–53 kcal/mol for the activation energy for homolysis of an "unstrained" **8** or **9**. Thus, if the **8** $\rightleftarrows$ **9** rearrangement proceeds exclusively via the diradical pathway, only 15–50% of the 18–20 kcal/mol[17] of the cyclopropane strain energy usually released in the transition state for cyclopropane rupture is realized in this process. Although the positive activation entropy ($\Delta S^{\ddagger} = +2$ eu) is suggestive of the diradical process,[2] this value is somewhat lower than that normally observed in the geometric isomerization of cyclopropanes (*cis*-1,2-dideuteriocyclopropane, +13 eu;[18] 1-methyl-*cis*-2,3-dideuteriocyclopropane, +10 eu,[19] and *cis*-1,2-dimethylspiro[2.4]hepta-4,6-diene, +8 eu[4]). Thus, it appears reasonable to conclude that both the stepwise and concerted processes may be involved in this rearrangement. The apparently exclusive preference for the concerted rearrangement in the pyrolysis of *cis*- and *trans*-6,9-dimethylspiro[4.4]nona-1,3-diene,[14] as evidenced by the high degree of stereospecificity of the rearrangement, is understandable in terms of the strained character of the bicyclo[3.2.0]heptadiene intermediate derived from the spiroheptadienes, an appreciable degree of which must be experienced in the transition state for concerted cyclopropyl methylene migration.

The present observations appear most adequately accommodated by a stepwise perambulation of the C_2H_4 fragment and a hydrogen atom about the periphery of the cyclopentadiene ring. Although the stepwise process appears operative, *competitive concerted [1,5]-sigmatropic methylene migration may obtain.*[20] The results of detailed stereochemical experiments currently in progress should provide the basis for clarification of the mechanism of [1,5]-carbon shifts in this spiroheptadiene system.

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R. A. Clark,* W. J. Hayles, D. S. Youngs
Department of Chemistry
Rochester Institute of Technology
Rochester, New York 14623

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$Rh_6(CO)_{16}$. A Homogeneous Catalyst for the Oxidation of Carbon Monoxide to Carbon Dioxide and for the Oxidative Cleavage of Carbon–Carbon Bonds in Ketones to Carboxylic Acids

Sir:

We wish to report the first example of a homogeneously catalyzed oxidation reaction with molecular oxygen and a transition metal cluster compound. We have found that the compound $Rh_6(CO)_{16}$ will catalyze both the oxidation of CO to CO_2 and the oxidation of ketones to carboxylic acids, by molecular oxygen. The CO is completely oxidized and the catalyst retains its initial activity even after 12,500 mmol of CO_2 have been produced.[1]

Previous work with mononuclear complexes of Rh(I),[2] or the compound $Pt(PPh_3)_4$,[3] has shown that CO can be oxidized with molecular oxygen in a homogeneously catalyzed system, but in both of these cases there is a concomitant oxidation of the ligand. In our case since the compound used is an unsubstituted carbonyl complex the catalyst is recovered unchanged from the reaction. An alternative procedure has been used by Halpern et al., who effected oxidation of a coordinated carbonyl by attack with hydroxide ion.[4] The oxidation of CO to CO_2 in the presence of $Rh_6(CO)_{16}$ can be carried out in acetone as solvent. The cluster compound is insoluble in this solvent at 25° and is recovered in crystalline form at the end of a reaction run. Nevertheless, the catalytic reaction takes place in solution since the compound is catalytically inactive in the absence of solvent or as a suspension in hexane. Final verification of the homogeneity of the active species was obtained by cooling the reaction vessel, filtering the solution, returning the filtrate to the reac-

Table I

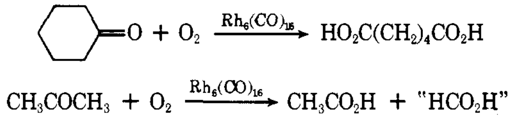
Solvent	Yield CO_2[a] (mmol)	Solvent oxidation	Remaining O_2 (%)
None	Trace	None	100
Cyclohexane	Trace	None	100
Cyclohexene	5	*b*	10
Acetone	20	CH_3CO_2H(1.5 mmol)	10
Cyclohexanone	17	$(CH_2)_4(CO_2H)_2$ (1 mmol)	10
Dimethoxyethane	9	*b*	20
Dimethyl sulfoxide[c]	10	*d*	10

[a] From CO (32 mmol) and O_2 (16 mmol). [b] Solvent decomposition to several unidentified compounds occurred. [c] No $Rh_6(CO)_{16}$ could be recovered, but the resulting solution remained catalytically active. [d] Unidentified acidic products were formed.

tion, and proceeding with the catalysis. Oxidation continued, and a homogeneous solution remained when the mixture was finally assayed.

In a typical reaction $Rh_6(CO)_{16}$ (~10^{-2} mmol) was suspended in 10 ml of solvent in a glass vial and the mixture stirred at 100° under a pressure of 34 atm (35 ml volume). The ratio of $CO:O_2$ was 2:1 and the reaction was complete within 24 hr. The quantities of CO_2 formed and O_2 remaining were measured by mass spectrometer, after thorough mixing of the vented gases with a known amount of argon. Gas quantities were obtained from the peak areas by comparison to a standard curve after contributions from interfering ions were subtracted out. The peaks used for these analyses were 32 for O_2, 40 for Ar, and 44 for CO_2.

The volume of O_2 consumed in acetone as solvent is in excess of that required for the conversion of the CO into CO_2. The other product, along with very minor unidentified components, is acetic acid. The acetic acid was identified by gas chromatography and assayed by titration. This homogeneous oxidation of acetone to acetic acid must occur by a catalytic C–C bond cleavage reaction. In order to identify the fate of the other methyl group on acetone the reaction was carried out in cyclohexanone as solvent. Oxidation of CO to CO_2 was again facile and the acid now formed was adipic acid. This result implies that the other product from acetone is formic acid, which would not be stable under the condition of the reaction. In order to increase the yield of adipic acid the reaction was carried out under the same total pressure but with a partial pressure ratio of 3:1 for O_2:CO. The yield of adipic acid in this run was 1000 mmol.[1] At the end of the reaction a red solution remained, but no $Rh_6(CO)_{16}$ was present. The hexameric cluster compound could be regenerated, however, by restoring a substantial pressure of CO and O_2 over this solution at 100°. Attempts to obtain the ketone oxidation under pure oxygen were unsuccessful due to decomposition of the cluster; nevertheless, $Rh_6(CO)_{16}$ could again be regenerated by the above procedure.



Previous work has shown that when $Rh_6(CO)_{16}$ is refluxed in acetic acid a dimer, $Rh_2(OAc)_2(CO)_4$, is obtained.[5] It appears therefore that under the conditions of our reaction there will be considerable conversion of the cluster into a carboxylate bridged dimer. In agreement with this rationale we have found that $Rh_2(OAc)_2(CO)_4$ is readily converted into $Rh_6(CO)_{16}$ under CO pressure. The carboxylate complex is not necessary for the catalytic conversion of CO into CO_2 since the reaction occurs in cyclohexene as solvent without any formation of acidic products. The oxidation of CO has been carried out in a range of solvents as shown in Table I.

When $Rh_2Cl_2(CO)_4$ was used as catalyst little conversion of CO to CO_2 occurred, and this corresponded with the formation of a small quantity of $Rh_6(CO)_{16}$. With $Rh_4(CO)_{12}$ catalysis was facile because of its ready conversion to $Rh_6(CO)_{16}$.

This work shows that the compound $Rh_6(CO)_{16}$ is effective as an oxidation catalyst in addition to being a useful hydrogenation and hydroformylation catalyst.[6-8] This oxidation reaction, however, is particularly interesting because of the accompanying unique homogeneously catalyzed C–C bond cleavage reaction of ketones.

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Gary D. Mercer, J. Shing Shu, Thomas B. Rauchfuss
D. Max Roundhill*
Department of Chemistry, Washington State University
Pullman, Washington 99163

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Nuclear Magnetic Resonance Study on Ligand–Metalloporphyrin Complexation. A Study of Equilibria and Paramagnetism in a Ferriprotoporphyrin–Cyanide System

Sir:

A large number of studies of the effect of ligands on the high to low spin transitions of ferrous and ferric porphyrins have been reported.[1-4] Despite the wide variety of NMR studies,[1,2] relatively little is known concerning the equilibria and kinetics of ligand binding to the iron of porphyrins. We report here a study of ferriprotoporphyrin (hemin)–cyanide complexation in DMSO-d_6[5] in which we show: (i) the cyanide ligation to hemin is a two-step binding process (see eq 1 and 2) with the binding constant K_1 greater than K_2 (see eq 3 and 4), (ii) the first step involves formation of the previously unknown monocyano adduct of hemin, paramagnetic susceptibility measurements show this adduct to be low