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Preliminary communication

ACTIVATION OF MOLECULAR OXYGEN. SELECTIVE OXIDATION OF TERMINAL OLEFINS AND ALCOHOLS CATALYZED BY CATIONIC COMPLEXES OF RHODIUM(I)

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Summary

Rhodium(I) complexes containing hybrid "hemilabile" ligands of general formula $[Rh(Ph_2PCH_2CH_2SR)_2]^+$ (R = Ph, Et, Me) are found to catalyze air oxidation of terminal olefins to the corresponding methyl ketones, of primary alcohols to acetals and of secondary alcohols to ketones.

Selective O_2-oxidation of olefins to ketones by dioxygen-metal complexes have been reported in the recent years. Both oxygen atoms can sometimes be transferred catalytically to the organic substrate [1—3], while in other cases only one oxygen atom is incorporated into the ketone, the other being reduced by a two-equivalent reducing agent, such as PPh_3 [4] or H_2 [5].

In this paper we report the successful catalytic oxidation of terminal olefins to methyl ketones, using acidic alcoholic solutions of rhodium(I) complexes with the hybrid bidentate ligands $Ph_2P(CH_2)_2SR$ (PSR; R = Ph, Et, Me), of the type $[Rh(PSR)_2]BF_4$. The above "hemilabile" ligands were chosen in order to produce highly reactive coordinatively unsaturated species in solution [6].

The yellow rhodium(I) complexes $[Rh(PSR)_2]BF_4$, prepared by a modification of the general procedure of Lewis [7], slowly react with molecular oxygen (30 min—1 h), when dissolved in common organic solvents, to give the corresponding 1/1 adducts $[Rh(PSR)_2O_2]BF_4$ (eq. 1). In some cases (R = Ph, Et),

$$[Rh(PSR)_2]^+ + O_2 \rightleftharpoons [Rh(PSR)_2O_2]^+ \qquad (1)$$

the peroxo-derivatives have been isolated in the solid state as tetraphenylbornate salts [8].

At room temperature and pressure, the $[Rh(PSR)_2O_2]^+$ complexes react with 1-alkenes, both in the absence and in the presence of solvent (dichloromethane, alcohols) to give small, substoichiometric amounts of the corresponding methyl ketones.

In the presence of added acid, the above oxygen transfer in alcohols becomes catalytic. Typically, ethanol or methanol solutions of $[Rh(PSPh)_2]BF_4$ (0.01—0.05 *M*) in the presence of at least a ten-fold excess of 1-octene and equivalent amounts of methanesulfonic acid, absorb molecular oxygen at 1 atm and 25° C, to catalytically generate 2-octanone. Reactions are slow, the turnover number being about one per day (in methanol; even less in ethanol), based on week-long experiments at 25° C. The rate significantly increases with the temperature, up to six turnovers per day, in methanol at 50° C or ethanol at 70° C.

Only terminal olefins (1-hexene, 1-octene, 1,7-octadiene) are catalytically oxidized; no reactions have been observed with internal olefins (4-octene, cyclohexene) and 1,5-cyclooctadiene.

Two other major products are formed catalytically during the reaction in ethanol, and have been identified by GLC-MS as vinyl ethyl ether and acetal. The amounts of vinyl ethyl ether and acetal parallel, but significantly exceed, that of the oxidation product of the olefins, and were found to be formed independently by metal-promoted oxidation of ethanol, as indicated by catalytic experiments carried out in the absence of olefin. The catalytic air-oxidation of methanol under the same conditions gives dimethoxymethane. Other alcohols (1-propanol, 1-butanol, 2-propanol and cyclohexanol) also undergo easy oxidation, to propionaldehyde dipropyl acetal, butyraldehyde dibutyl acetal, acetone, and cyclohexanone, respectively.

None of the catalytic systems described above lose their activity even after several weeks at temperatures near the boiling points of the solvents: significantly there is no evidence of ligand oxidation in the IR spectra of the reaction residues, i.e. there are no absorptions attributable to PO and/or SO or SO_2 moieties. This contrasts with the ready oxidation of the ligands in related systems, such as $[RhCl(PPh_3)_3]$ [4,9,10] or $[Rh(AsPh_3)_4]^+$ [11], which results in the absence of rapid loss of catalytic activity.

Closely related results are obtained with other $[Rh(PSR)_2]BF_4$ complexes (R = Me, Et), except that the formation rates of the methyl ketones are definitely lower. The diphosphine derivative of rhodium(I) $[Rh(dppe)_2]BF_4$ (dppe = 1,2-diphenylphosphinoethane) behaves differently and erratic induction times (up to 24 h) have been observed for the catalytic processes. However, apart from the induction times, $[Rh(dppe)_2]BF_4$ is found as effective as $[Rh(PSPh)_2]BF_4$ for air-oxidation of terminal olefins to methyl ketones and of alcohols to ketones or acetals. In this case, again no evidence of massive oxidation of the ligand was obtained.

The simultaneous but independent oxidation of olefins and alcohols makes it difficult to correlate the amounts of absorbed dioxygen with those of produced methyl ketones, thus precluding an answer to the important question concerning the catalytic process, namely whether or not both oxygen atoms are transferred to the olefin. A comparison of the amount of 2-octanone formed with that of dioxygen absorbed, roughly corrected for the portion involved in the oxidation of ethanol, leads to the very preliminary conclusion that both oxygen atoms are taken up by 1-octene.

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