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HETEROPOLY ANION-ASSISTED Rh CATALYSIS REVEALED IN THE HOMOGENEOUS SELECTIVE HYDROGENATION

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When coupled with lithium salt of heteropoly acid, the Wilkinson complex $RhCl(PPh_3)_3$ catalyst became very active and selective for the semihydrogenation of alkyne to alkene and, more interestingly, exhibited sharp substrate-selectivity in hydrogenation of substituted alkenes.

In recent years the Keggin-type heteropoly acid (abbreviated as HPA) has been actively applied as catalyst to various organic reactions, because it possesses dual catalytic function of strong acidity and oxidizing ability. We have also studied the homogeneous catalyses of HPA in order to elucidate its catalytic features at a molecular level. Through our previous studies,1-4) we think now that these interesting catalytic behaviors by HPA are undoubtedly due to the intrinsic (electronic and structural) properties of heteropoly anion, or the conjugate base of HPA. We already reported that heteropoly anion revealed an excellent modifying effect on palladium in catalytic acetylenic semihydrogenation.5) In this letter, a further attempt of modifying rhodium such as the Wilkinson complex, $RhCl(PPh_3)_3$, with heteropoly anion will be presented on the homogeneous hydrogenation of alkynes and alkenes.

All experiments were performed in a liquid-phase closed system at 30 °C. The homogeneous catalyst solution was prepared by dissolving $RhCl(PPh_3)_3$ (4 mM) and lithium salt of HPA (20 mM) in a well deoxygenated benzene-ethanol (1:1) solvent under hydrogen atmosphere. After the completion of hydrogen uptake, 0.4 M of the substrate was fed into the solution, and the hydrogenation reaction was initiated under 1 atm of hydrogen. A small portion of the solution was withdrawn periodically and analyzed by means of GLC.

Table 1 shows the results of the hydrogenation of 1-phenyl-1-propyne by the Rh catalysts consisting of $RhCl(PPh_3)_3$ and lithium salts of oxoacids. Higher activity and selectivity of semihydrogenation to β-methylstyrene was obtained only when either $Li_4SiW_{12}O_{40}$ or $LiClO_4$ was added. These catalysts were also effective for the semihydrogenation of phenylacetylene to styrene under the same conditions. Considering that a cationic Rh complex such as $[Rh(diene)L_n]^+ClO_4^-$ (L:ligand) is an excellent catalyst for the selective semihydrogenation of alkyne to alkene,6) it is probable that, also in this case, a cationic species of $[(RhH_2(PPh_3)_xS_y)^+]_n A^{n-}$ (S:solvent, A^{n-}:ClO_4^- or $SiW_{12}O_{40}^{4-}$) is formed by the reaction of $RhCl(PPh_3)_3$ with $LiClO_4$ or $Li_4SiW_{12}O_{40}$ under H_2 atmosphere to work as an active catalyst. In fact, it was observed qualitatively that chloride ion was liberated by the reaction

Table 1. Hydrogenation of 1-phenyl-1-propyne with $RhCl(PPh_3)_3$ a)

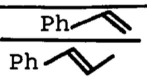
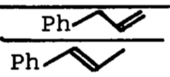
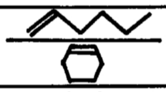
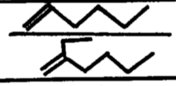
Additive	Time h	Conv. %	β-Methylstyrene selectivity / mol%
none	6.0	47	49
$Li_4SiW_{12}O_{40}$	1.1	97	84
$Li_4SiMo_{12}O_{40}$	1.1	93	67
$LiClO_4$	0.7	91	83
$LiNO_3$	2.3	43	75

a) H_2 1 atm, 30 °C, C_6H_6-EtOH (1:1) solvent, $RhCl(PPh_3)_3$ 4 mM, additive 20 mM, substrate 0.4 M.

of $RhCl(PPh_3)_3$ and $Li_4SiW_{12}O_{40}$ in an atmosphere of hydrogen, although the cationic complex could not be isolated. The tungstosilicate anion was hardly reduced with hydrogen at 30 °C even in the presence of Rh complex, whereas the molybdosilicate anion was readily reduced to form the so-called "heteropoly blue" absorbing 1.5 mol of hydrogen per mol of the Keggin unit.

More interestingly, the Rh catalyst system containing $SiW_{12}O_{40}{}^{4-}$ is very effective for the substrate-selective hydrogenation of substituted alkenes. Table 2 lists the comparative rates of hydrogenation of mono- and disubstituted ethenes by the Rh catalysts modified with various lithium salts. The $SiW_{12}O_{40}{}^{4-}$ system specifically retarded the hydrogenation of more crowded 1,2- or 1,1-disubstituted ethene, although its overall catalytic activity of hydrogenation is lower than those of $RhCl(PPh_3)_3$ itself and the other modified systems. This substrate-selective ability is obviously due to a modifying effect of $SiW_{12}O_{40}{}^{4-}$ anion. Probably $SiW_{12}O_{40}{}^{4-}$ anion having a large polyhedron structure exists near the coordination sphere as a counter anion of the cationic Rh complex, and sterically hinders the access of a bulky alkene molecule to the Rh cation.

Table 2. Comparative rates of hydrogenation of alkenes by $RhCl(PPh_3)_3$ catalyst a)

Additive				
none	1.2	1.6	1.1	3.2
$Li_4SiW_{12}O_{40}$	6.4	3.9	3.8	6.2
$Li_4SiMo_{12}O_{40}$	1.5	1.9	1.9	2.8
$LiClO_4$	1.5	1.1	1.0	3.5

a) The reaction conditions are the same as indicated in Table 1.

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