Refuxing azoimine ligand contg. terminal acetylene group (L = C\(_6\)H\(_5\)N=N-C(OCH\(_3\))=N-C\(_6\)H\(_4\)C≡CH) with RuCl\(_3\)·3H\(_2\)O in ethanol resulted hydrating the terminal acetylene group to the corresponding enol form C\(_6\)H\(_5\)N=N-C(OCH\(_3\))=N-C\(_6\)H\(_4\)C(OH)=CH\(_2\) (L1), ketone form C\(_6\)H\(_5\)N=N-C(OCH\(_3\))=N-C\(_6\)H\(_4\)COCH\(_3\) (L2) and vinyl chloride: C\(_6\)H\(_5\)N=N-C(OCH\(_3\))=N-C\(_6\)H\(_4\)C(Cl)=CH\(_2\) (L3) via Markovnikov selectivity. Ruthenium complexes of the later ligands and \(\alpha\)-diamines trans-[Ru(N-N)(Y)Cl\(_2\)] (Y = L1, N-N = 4,4'-dimethoxy-2,2'-bipyridine; dmeb (1), 1,10-phenanthroline; phen (2), 3,4,7,8-tetramethyl-1,10-phenanthroline; tmphen (3), Y = L2, N-N = dmeb (4), phen (5), tmphen (6)) were synthesized from L, N-N ligands and RuCl\(_3\)·3H\(_2\)O. Complexes 1-6 were characterized by spectroscopic (IR, UV-visible, \(\text{^1}H, \text{^13}C\) NMR, DEPT-135) and electrochem. techniques. The crystal structures of trans-[Ru(tmphen)(L1)Cl] (3) and trans-[Ru(bpy)(L3)Cl] (7) were detd. and found to have distorted octahedral geometry. The catalytic activity of 3 towards the hydration of cinnamaldehyde is reported.