STRUCTURE OF A NEW HYDRIDO-(METHOXY)-IRIDIUM(III) COMPLEX RELATED TO CATALYTIC REDUCTION OF ALKynes. Tsuneaki Yamagata, Kazuhide Tani, Department of Chemistry, Faculty of Engineering Science, Osaka University

Hydrido(alkoxy) complexes of transition metals play important roles of catalytic processes involving hydrosy transfer and alcohol homologation. Here we report the preparation and structural characterization of a new dinuclear hydrido(methoxy)iridium(III) complex.

The hydrido(methoxy) complex, [(Ir([R]-binap)(H)(O)-OMe)-(Ir-[R]-binap)]Cl (1)-CH$_2$OH (I) was prepared by treating "Ir([R]-binap)Cl" ([R]-binap = (R)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) in absolute methanol-toluene (1:1). The structure of 1 was determined by an X-ray crystallography and NMR investigation. The cationic part of $\text{I}$ has a dinuclear iridium. The coordination environment of both iridium atoms can be described as a distorted octahedron with two bridging methoxy and a chloride ligands and a terminal hydride ligand. The bridging chlorine atom of the cationic part and the oxygen and carbon atoms of the solvating methanol lay on a 2-fold axis. The chloride counter anion locates near the methanol. The dihedral angle between two least-squares planes defined by two phosphorus atoms of BINA and two oxygen atoms of bridging methoxy ligands is 142.0(1)$^\circ$. A terminal hydride ligand occupied trans position to the a-chloro ligand and cis position to the methoxy groups. The 31P([H]) NMR spectrum shows two doublets (AB coupling pattern) at $\delta$ -1.75 and -15.22 ($J = 19$ Hz). The $\text{H}$ NMR spectrum showed the terminal hydride at $\delta$ -23.10 (doublet of doublets, $J = 18$, 23 Hz) and the methoxy groups at $\delta$ 2.63 (triplet, $J = 3.4$ Hz). These results are consistent with the X-ray structure and show that 1 is prepared by oxidative addition of methanol to the neutral Ir(III) complex. A series of new complexes of divalent iron(II) with 1,3-diketones was prepared and characterized. The complex Fe(1,3-diketonato)Cl$_2$ has been prepared and characterized. The coordination environment of the iron(II) atom is described as a distorted octahedron with two bridging diketonate ligands and a chloride ligand. The dihedral angle between two least-squares planes defined by two chromium atoms of BINA and two oxygen atoms of bridging diketonate ligands is 142.0(1)$^\circ$. A terminal chloro ligand occupied trans position to the a-diketo ligand and cis position to the methoxy group. The 31P([H]) NMR spectrum shows a triplet at $\delta$ -1.75 (d, $J = 19$ Hz). The $\text{H}$ NMR spectrum showed the terminal chloro at $\delta$ 2.63 (triplet, $J = 3.4$ Hz). These results are consistent with the X-ray structure and show that 1 is prepared by oxidative addition of chloro to the neutral Ir(III) complex.