Metal expansion of dinuclear complexes of group 7 on the basis of PH-acidic ligands: synthesis, structures, properties and catalysis

Abstract

The aim of this dissertation was the development of metal expansion reactions for PH-functionalised cluster complexes. Deprotonation of $Re_2(CO)_9(PH_2R)$ (R = H, Cy) and subsequent addition of $BrMCp(CO)_2$ (M = Fe, Ru) gave the trinuclear cluster complexes $Re_2(CO)_9(\mu\text{-}PHR(MCp(CO)_2))$ (R = H, Cy, M = Fe, Ru). The tetranuclear cluster complexes $Re_2(CO)_9(\mu_3\text{-}PH(FeCp(CO)_2)_2)$ and $Re_2(CO)_9(\mu_3\text{-}PH(Fe(cis\text{-}Cp)CO)_2(\mu\text{-}CO))$ were analogously obtained by twofold metalation of $Re_2(CO)_9(PH_3)$. The behavior of the prepared cluster complexes under UV-irradiation or heating was studied as well. The monometalated cluster complexes of the type $Re_2(CO)_9(\mu\text{-}PHR(MCp(CO)_2))$ gave hydrido phosphido bridged cluster complexes of the type $Re_2(\mu\text{-}H)(\mu_3\text{-}PR(MCp(CO)_2))(CO)_8$. The twofold metalated substances yielded under the same reaction conditions the isomers $Re_2(\mu\text{-}H)(\mu_4\text{-}P(Fe(trans\text{-}Cp)CO)_2(\mu\text{-}CO))(CO)_8$ and $Re_2(\mu\text{-}H)(\mu_4\text{-}P(Fe(cis\text{-}Cp)CO)_2(\mu\text{-}CO))(CO)_8$. Selected cluster complexes were expanded by isolobal replacement of a μ-H ligand by an $AuPPh_3$-fragment. Moreover $Re_2(\mu\text{-}H)(\mu_4\text{-}P(Fe(cis\text{-}Cp)CO)_2(\mu\text{-}CO))(CO)_8$ was deprotonated. Redoxcondensation of the resulting anion $[Re_2(\mu_4\text{-}P(Fe(cis\text{-}Cp)CO)_2(\mu\text{-}CO))(CO)_8]^-$ with $Rh(COD)^+$ gave the pentanuclear cluster complex $Re_2Rh(\mu_4\text{-}P(Fe(cis\text{-}Cp)CO)_2(\mu\text{-}CO))(\mu\text{-}CO)_2(CO)_8$ in good yield. The catalytic activity of the latter with respect to hydroformylation of cyclohexene was studied by gas chromatography and compared to the activity of the similar complex $Re_2Rh(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_8$.