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Synthesis, Chemical and Catalytic Properties of Transition Metal Complexes with Polydentate Phosphine Ligands

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Abstract

The linear chiral triphosphine ligand (S,S)-PhP(CH₂C*HMeCH₂PPh₂)₂, ttp*, was synthesized by the reaction of (S)-Ph₂PCH₂CHMeCH₂Cl and PhPH₂ in the presence of LDA. Treatment of [RhCl(COD)]₂ with ttp* produced RhCl(ttp*). Reaction of RuCl₂(PPh₃)₃ or RuCl₂(DMSO)₄ with ttp* gave RuCl₂(ttp*). Reaction of CoCl₂ with ttp* in methanol gave CoCl₂(ttp*). Treatment of RhCl(ttp*) and RuCl₂(ttp*) with NaBH₄ led to Rh(BH₄)(ttp*) and RuH(η²-BH₄)(ttp*) respectively. The tripodal chiral triphosphine ligand (R)-Ph₂PCH₂CH(PPh₂)CH₂CH₂PPh₂, etp* was synthesized by the reaction of (S)-MsOCH₂CH(OMs)CH₂CH₂OMs with KPh₂P. Reaction of RuCl₂(DMSO)₄ and etp* gave RuCl(etp*). A series of ruthenium complexes with the orthometallated ligand [2,6-(PhP₂CH₂)₂C₆H₃]- (PCP) were synthesized. Reaction of RuCl₂(PPh₃)₃ with 1,3-(Ph₂PCH₂)₂C₆H₄ produced the coordinatively unsaturated complex RuCl(PPh₃)(PCP), which was characterized by X-ray crystallography. Treatment of RuCl(PPh₃)(PCP) with 4-phenylpyridine (pyph) yielded RuCl(pyph)(PPh₃)(PCP). Treatment of RuCl(PPh₃)(PCP) with PMe₃ and CO generated RuCl(PMe₃)₂(PCP) and RuCl(CO)₂(PCP), respectively. Reactions of RuCl(PPh₃)(PCP) with NaH in THF and NaBH₄ in methanol gave RuH(PPh₃)(PCP) and RuH(CO)(PPh₃)(PCP), respectively. The hydride complex RuH(PMe₃)₂(PCP) was prepared by the reaction of RuCl(PMe₃)₂(PCP) with NaBH₄. Reaction of RuCl(PPh₃)(PCP) with NaBH₄ in THF produced an orange compound which can be formulated as a BH₃ complex RuH(BH₃)(PPh₃)(PCP) (A). RuH(BH₃)(PPh₃)(PCP) (A) isomerized to RuH(BH₃)(PPh₃)(PCP) (B) in solution. Treatment of RuH(BH₃)(PPh₃)(PCP) (A) with CO produced a mixture of RuH(CO)(PPh₃)(PCP) and RuH(CO)₂(PCP). Reaction of RuH(BH₃)(PPh₃)(PCP) (A) with PMe₃ gave RuH(PMe₃)(PPh₃)(PCP). Treatment of RuH(BH₃)(PPh₃)(PCP) (B) with CO and PMe₃ led to

$\text{RuH}(\text{CO})(\text{PPh}_3)(\text{PCP})$ and $\text{RuH}(\text{PMe}_3)(\text{PPh}_3)(\text{PCP})$ respectively. Reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ ($\text{PCP} = 2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3$) with $\text{PhC}[\text{is equivalent to}]\text{CH}$ and $\text{HC}[\text{is equivalent to}]\text{CC}(\text{OH})\text{Ph}_2$ gave the unusual coupling products $\text{RuCl}(\text{PPh}_3)(\eta^4\text{-PhCH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ and $\text{RuCl}(\text{PPh}_3)(\eta^4\text{-Ph}_2\text{C}(\text{OH})\text{CH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$, respectively.

$\text{RuCl}(\text{PPh}_3)(\eta^4\text{-PhCH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ was characterized by X-ray crystallography. Dehydration was observed in the coupling reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with $\text{HC}[\text{is equivalent to}]\text{CC}(\text{OH})\text{PhMe}$ and $\text{HC}[\text{is equivalent to}]\text{C-cyclo-C}_6\text{H}_{10}(\text{OH})$. Thus the coupling products

$\text{RuCl}(\text{PPh}_3)(\eta^4\text{-CH}_2=\text{CPhCH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ and

$\text{RuCl}(\text{PPh}_3)(\eta^4\text{-cyclo-C}_6\text{H}_9\text{-CH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ were obtained from the reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with $\text{HC}[\text{is equivalent to}]\text{CC}(\text{OH})\text{PhMe}$ and $\text{HC}[\text{is equivalent to}]\text{C-cyclo-C}_6\text{H}_{10}(\text{OH})$, respectively. Treatment of

$[\text{Ru}(\text{PMe}_3)_2(\text{PCP})]\text{BF}_4$ with $\text{PhC}[\text{is equivalent to}]\text{CH}$ produced

$[\text{Ru}(\text{PMe}_3)_2(\eta^4\text{-PhCH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)]\text{BF}_4$. Reaction of

$\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with $\text{PhC}[\text{is equivalent to}]\text{CLi}$ gave $\text{Ru}(\text{C}[\text{is equivalent to}]\text{CPh})(\text{PPh}_3)(\text{PCP})$. Protonation of this acetylide complex in the presence of Cl^- produced the coupling product $\text{RuCl}(\text{PPh}_3)(\eta^4\text{-PhCH}=\text{C-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$

along with some uncharacterized species. Treatment of $\text{RuCl}_2(\text{PPh}_3)_3$ with PMP ($\text{PMP} = 2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_5\text{H}_3\text{N}$) in acetone produced $\text{RuCl}_2(\text{PPh}_3)(\text{PMP})$ which has been characterized by X-ray diffraction. Treatment of $\text{RuCl}_2(\text{PPh}_3)(\text{PMP})$ with NaBH_4 in methanol gave $\text{RuHCl}(\text{PPh}_3)(\text{PMP})$, acidification of which with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ produced the molecular dihydrogen complex

$[\text{RuCl}(\text{H}_2)(\text{PPh}_3)(\text{PMP})]\text{BF}_4$. Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with PMP in

benzene produced $\text{RuHCl}(\text{CO})(\text{PMP})$ which reacted with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to give the molecular dihydrogen complex $[\text{RuCl}(\text{H}_2)(\text{CO})(\text{PMP})]\text{BF}_4$. The osmium

molecular dihydrogen complex $[\text{OsCl}(\text{H}_2)(\text{PPh}_3)(\text{PMP})]\text{BF}_4$ was prepared by protonation of $\text{OsHCl}(\text{PPh}_3)(\text{PMP})$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. Relative acidities of the dihydrogen complexes were investigated by NMR spectroscopy of equilibration reactions conducted in CD_2Cl_2 . $[\text{RuCl}(\text{H}_2)(\text{CO})(\text{PMP})]\text{BF}_4$ is more acidic than $[\text{RuCl}(\text{H}_2)(\text{PPh}_3)(\text{PMP})]\text{BF}_4$ which is in turn more acidic than its osmium

analog $[\text{OsCl}(\text{H}_2)(\text{PPh}_3)(\text{PMP})]\text{BF}_4$. The catalytic properties of

$\text{RuH}(\eta^2\text{-BH}_4)(\text{ttp})$, $\text{RuCl}_2(\text{ttp})$, $\text{RhCl}(\text{ttp}^*)$, $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ and $\text{RuCl}_2(\text{PPh}_3)(\text{PMP})$ for hydrogenation of styrene have been tested.

$\text{RuH}(\eta^2\text{-BH}_4)(\text{ttp})$ and $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ are very efficient catalysts and

quantitative yield of ethylbenzene was obtained in 20 min. $\text{RuCl}_2(\text{PPh}_3)(\text{PMP})$

has a relatively poor activity. The catalytic properties of $\text{RuCl}_2(\text{ttp}^*)$, $\text{RhCl}(\text{ttp}^*)$, $\text{Rh}(\text{BH}_4)(\text{ttp}^*)$, $\text{RuH}(\eta^2\text{-BH}_4)(\text{ttp}^*)$ and $\text{RuCl}_2(\text{etp}^*)$ for the asymmetric

hydrogenation of α -acetamidocinnamic acid have been tested. $\text{RuCl}_2(\text{ttp}^*)$, $\text{RhCl}(\text{ttp}^*)$, $\text{Rh}(\text{BH}_4)(\text{ttp}^*)$ and $\text{RuH}(\eta^2\text{-BH}_4)(\text{ttp}^*)$ are efficient catalysts and quantitative production of N-acetyl-(S)-phenylalanine could be obtained after 24 hrs. However, the optical yield is moderate and in the range of 2-50%. The catalytic properties of $\text{RuCl}_2(\text{ttp}^*)$, $\text{RuCl}_2(\text{etp}^*)$, $\text{RuCl}_2(\text{pigiphos})$, $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ for cyclopropanation were investigated using styrene and ethyl diazoacetate as the substrates. The yields for cyclopropanation products are relatively low and the major products are diethyl fumarate and diethyl maleate. The cis/trans ratio for the cyclopropanation product is moderate and the optical yields for the reactions are low. Reaction of $\text{RuCl}_2(\text{ttp}^*)$ with ethyl diazoacetate produced $\text{RuCl}_2(\text{ttp}^*)(=\text{CHCO}_2\text{Et})$, which in reactions with ethyl diazoacetate and styrene produced the dimerization and cyclopropanation products respectively.