

H-Spirophosphoranes as Ligands in Ruthenium-Catalyzed Hydrogen Transfer Reaction

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Streszczenie

A group of ruthenium(II) complexes stabilized by the tautomeric forms of H-spirophosphorane ligands $\text{HP}(\text{OCH}_2\text{CMe}_2\text{NH})_2$ **L1** and $\text{HP}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{OCH}_2\text{CMe}_2\text{NH})$ **L2** was prepared from various precursors. Starting with $[\text{RuCl}_2(\text{DMSO-S})_3(\text{DMSO-O})]$, two complexes, $[\text{RuCl}_2\{\text{P}(\text{OCH}_2\text{CMe}_2\text{NH})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}(\text{DMSO})_2]$ **[Ru1L1]** and $[\text{RuCl}_2\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}(\text{DMSO})_2]$ **[Ru2L2]**, were obtained. The treatment of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with phosphorane ligands in acetonitrile produces $[\text{RuCl}_2\{\text{P}(\text{OCH}_2\text{CMe}_2\text{NH})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}(\text{MeCN})(\text{PPh}_3)]$ **[Ru3L1]** and $[\text{RuCl}_2\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}(\text{MeCN})(\text{PPh}_3)]$ **[Ru4L2]**. However, when the reaction was conducted in dichloromethane with excess ligands **L1** or **L2**, diastereomers of $[\text{RuCl}_2\{\text{P}(\text{OCH}_2\text{CMe}_2\text{NH})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}_2]$ **[Ru5L1]** and $[\text{RuCl}_2\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}_2]$ **[Ru6L2]** were obtained. Two additional diastereomers of the latter complexes were prepared starting with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$. Finally, the equimolar reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ and **L1** in dichloromethane resulted in the formation of the dimer $[\text{Ru}(\mu\text{-Cl})\text{Cl}\{\text{P}(\text{OCH}_2\text{CMe}_2\text{NH})(\text{OCH}_2\text{CMe}_2\text{NH}_2)\}(\text{PPh}_3)]_2$ **[Ru7L1]**. The resulting complexes were analyzed using a variety of analytical techniques, including multinuclear nuclear magnetic resonance, infrared spectroscopy, single-crystal X-ray diffraction, and elemental analysis. Density functional theory (DFT) calculations were employed to evaluate the stability of the complexes. Subsequently, well-defined catalyst precursors were assessed in the hydrogen transfer reaction. The catalyst **[Ru1L1]** demonstrated excellent activity toward the formation of aromatic alcohols in the hydrogen transfer reaction from 2-propanol to aromatic ketones.

Słowa kluczowe

Density functional theory (DFT) calculations, Phosphorus ligands, Ruthenium complexes, Hydrogen transfer reaction, X-ray structure

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