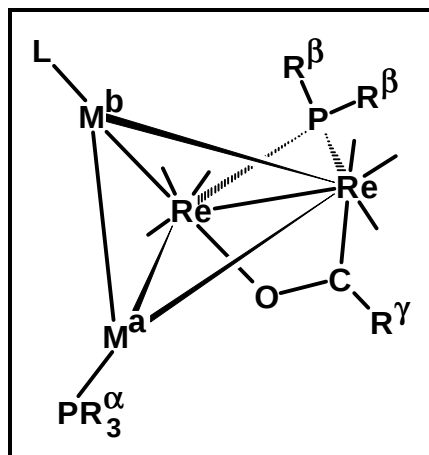


The Introduction of Chiral Auxiliaries in Asymmetric Rhenium Gold Cluster Complexes



This Work is aimed at the synthesis and examination of properties of asymmetrical metal cluster complexes. To suppress dynamic behaviour in such compounds different bridging ligands always together with a diorganylphosphido group were introduced. The mechanistical pathway in the preparation of phosphido-acyl bridged complexes via reaction of $\text{Re}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_8$ with two equivalents of RLi ($\text{R} = \text{Bu}, \text{Ph}$) was studied in detail. Auration of the generated dianion with ClAuPPh_3 resulted in metalatetrahedrons of the type $\text{Re}_2(\text{AuPPh}_3)_2(\mu\text{-PCy}_2)(\mu\text{-C(R)O})(\text{CO})_6$ (s. Figure) A hydrido-bridged anionic complex type which was received from the dialkyl-addukt by an air oxidation process, was characterized by X-ray structure analysis for $\text{R} = \text{Bu}$. The transfer of this synthesis to relatively weak oxygen and nitrogen nucleophils succeeded by reactions of $\text{Re}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_7(\text{THF})$ with one equivalent of alkoxid or lithiumamid. The auration of this complex type yielded novel trinuclear cluster compounds containing a $\mu_3\text{-H}$ bridging proton (Fig.: $\text{MP}^\alpha_3 = \text{H}$).

The chiral modification of the bridging acylligands in above mentioned C_1 - symmetrical cluster compounds (Fig.: R^γ) was done by the use of $\text{Li(S)-2-methoxymethylpyrrolidinamide}$ as the reagent for the nucleophilic attack. Moreover the introduction of chiral auxiliaries in the position of the phosphido-ligand (Fig.: R^β) succeeded with $\text{Re}_2(\mu\text{-H})(\mu\text{-PMe}_2)(\text{CO})_8$ as the edukt in analogous syntheses. Finally $\text{Re}_2(\text{HgPPh}_2\text{Me})(\mu\text{-PCy}_2)(\mu\text{-C(Bu)O})(\text{CO})_6$ was prepared to be a model compound with chiral substituents at the terminally bonded phosphane. In that cluster the

two-valent mercury unit replaces two one-valent gold complex fragments of the tetrahedrons. ^{31}P -NMR-spectra proved the formation of diastereomeric pairs because of corresponding signal splittings, e. g. 2,5 ppm for the $\mu\text{-P}$ -atom in $\text{Re}_2(\text{AuPPh}_3)_2(\mu\text{-PMe}_2)(\mu\text{-C}(\text{Bu})\text{O})(\text{CO})_6$. This compound showed a diastereomeric excess of 27 % in chloroform solution. In contrast to that, the solid state was found consisting of only one (C)-configured isomer by means of X-ray structure analysis. These results were due to a permanent framework racemization in solution. The substitution of PPh_3 by PCy_3 diminished the isomerization rate to such an extent that a chromatographic separation followed by the determination of activation parameters could be reached. The value of $\Delta H^\ddagger$ was determined to be 84(2) kJ/mol, the corresponding inversion of the acylligand proceeds concerted.

A newly developed synthetic path to receive three electron donor ligands other than acyl used the photochemically induced conversion of a terminal at rhenium atoms η^1 -bonded substituents to the bridge bonding mode. By this way symmetrically carboxylatbridged metalatetrahedrons $\text{Re}_2(\text{AuPPh}_3)_2(\mu\text{-PCy}_2)(\mu\text{-OC}(\text{R})\text{O})(\text{CO})_6$ with several groups R could be obtained for the comparison with the C_1 -cluster complexes. For a chiral modification (+)-camphanat und (-)-prolinat were introduced. ORD measurements of all chiral substituted tetrahedrons showed considerably higher optical rotation compared to the auxiliaries alone (e. g. . $\Phi_D^{20} = -1277^\circ\text{cm}^2 \text{ kmol}^{-1}$ for $\text{Re}_2(\text{AuPCy}_3)_2(\mu\text{-PMe}_2)(\mu\text{-C}(\text{Bu})\text{O})(\text{CO})_6$ with regard to $\Phi_D^{20} = -92^\circ\text{cm}^2 \text{ kmol}^{-1}$ for (-)-menthylchlorid). The determination of Cotton effects in the CT region of the framework failed because of a great absorption of the UV irradiation used for ORD measurement. The possibility to extend the photochemical formation to further ligand bridges was shown by the preparation of halogeno and phthalimido complexes for both the metalatetrahedron and the $\mu_3\text{-H}$ -cluster type. With regard to a heterometallic modification of the tetrahedron cluster compounds the metal complex fragment $[\text{HgMoCp}(\text{CO})_3]$ was used to build up $\text{Re}_2(\text{AuPPh}_3)(\text{HgMoCp}(\text{CO})_3)(\mu\text{-PCy}_2)(\mu\text{-C}(\text{Bu})\text{O})(\text{CO})_6$. The positions M^a and M^b (s. Figure) were occupied with clearly increased regioselectivity than by pure combinations of group 11 elements used in previous attempts.