

Oxidation of 1-methyl-1-phenylhydrazine with oxidovanadium(V)—salan complexes : insight into the pathway to the formation of hydrazine by vanadium nitrogenase.

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Streszczenie

A series of oxidovanadium(V) complexes $[\text{VO}(\text{L}-\kappa^4\text{O},\text{N},\text{N},\text{O})(\text{OR})]$ (1a, R = Et, L = L1; 1b, R = Me, L = L1; 2, R = Me, L = L2; 3, R = Me, L = L3) were synthesized by the σ -bond metathesis reaction between $[\text{VO}(\text{OR})_3]$ and the linear diaminebis(phenol) derivatives H2L (salans) containing different para-substituents on the phenoxo group $[\text{CMe}_3\text{CH}_2\text{CMe}_2]$, L1; Me, L2; Cl, L3]. As shown by X-ray crystallography complexes 1a, 1b, and 2 exhibit cis- α geometry, do have a stereogenic vanadium center, and exist as a racemic mixture of the Δ cis- α and Λ cis- α enantiomers. In solution, as demonstrated by ^1H and ^{51}V NMR investigations, the structures of complexes 1–3 are consistent with their solid state. The reactions of 1b, 2, and 3 with NH_2NMePh in n-hexane afforded the oxidovanadium(IV) $[\text{VO}(\text{L}-\kappa^4\text{O},\text{N},\text{N},\text{O})]$ (4, L1; 5, L2; 6, L3) and 1,4-dimethyl-1,4-diphenyl-2-tetrazene ($\text{Me}_2\text{Ph}_2\text{N}_4$) (7) as the main products together with a small amount of hydrazido(2-) vanadium(V) $[\text{V}(\text{L}3-\kappa^4\text{O},\text{N},\text{N},\text{O})(\text{NNMePh})(\text{OMe})]$ (8). Proposed reaction course for the oxidation of NH_2NMePh by 1b–3 is discussed. Compounds 4–8 were characterized by chemical and physical techniques including the X-ray crystallography for 4, 7, and 8. The solid-state (powder) electron paramagnetic resonance spectra and magnetic features strongly indicate that complexes 4–6 are formed as a mixture of a mononuclear ($S = 1/2$) and a dinuclear ($S = 1$) species.

Adres publiczny

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<https://www.acs.org/content/acs/en.html>