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THE INTERACTION OF NIOBIUM AND VANADIUM CYCLOPENTADIENYL COMPLEXES WITH SUBSTITUTED HYDRAZINES

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Abstract—The hydrazido(1−) complexes $[V(\eta^5\text{-}C_5H_5)Cl_2(NRNR_2)]$ and $[Nb(\eta^5\text{-}C_5H_5)Cl_3(NRNR_2)]$ ($NRNR_2 = NMeNMe_2$ or $NPhNH_2$) were synthesized by reaction of $[V(\eta^5\text{-}C_5H_5)Cl_3]$ or $[Nb(\eta^5\text{-}C_5H_5)Cl_4]$ with either the lithium- or trimethylsilyl-substituted hydrazine. The interaction of $[V(\eta^5\text{-}C_5H_5)Cl_3]$ with diphos (diphos = dppe or dmpe) in Et_2O yields the adducts $[V(\eta^5\text{-}C_5H_5)Cl_3(\text{diphos})]$. Complexes such as $[Nb(C_5H_5)(\text{diphos})_2]$ and $[V(C_5H_5)Cl(\text{diphos})]$ are the reaction products of the reduction under N_2 of $[Nb(\eta^5\text{-}C_5H_5)Cl_4]$ and $[V(\eta^5\text{-}C_5H_5)Cl_3]$, either with Na(Hg) or Mg in the presence of phosphines or diphosphines. No stable dinitrogen complexes were isolated.

The reaction of $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ with trimethylsilyl-substituted hydrazines allows the isolation of hydrazido(1−) complexes, $[Ti(\eta^5\text{-}C_5H_5)Cl_2(NRNR_2)]$ ($NRNR_2 = NMeNMe_2$, NH_2NPh, $NHNMe_2$, etc.), which exhibit side-on coordination of the hydrazine fragment.[1,2] We also prepared complexes containing ligands such as RNN^- or R_2NN^{2-}, which correspond to putative intermediates in the process of conversion of dinitrogen to ammonia and/or hydrazine.

The recent discovery of a vanadium-containing nitrogenase[3] prompted us to extend this work to vanadium, and also to niobium.

The starting material, $[V(\eta^5\text{-}C_5H_5)Cl_3]$, is not as easily accessible as $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$.[4] We eventually optimized a three step synthesis pattern for the preparation of $[V(\eta^5\text{-}C_5H_5)Cl_3]$ in reasonable yields.

$[V(\eta^5\text{-}C_5H_5)Cl_3]$ reacts with trimethylsilyl-substituted hydrazines to give the hydrazido(1−) complexes $[V(C_5H_5)Cl_2(NRNR_2)]$, which have been characterized by IR and EPR spectroscopy, and by analyses. The phosphineiminate complex, $[V(C_5H_5)Cl_2(NPPh_3)]$, can be prepared in an analogous fashion from $[V(C_5H_5)Cl_3]$ and $Me_3SiNPPh_3$. Side-on coordination is expected in the hydrazide(1−) complexes, as occurs with titanium compounds, but end-on coordination is likely for $[V(\eta^5\text{-}C_5H_5)Cl_2(NPPh_3)]$, due to the bulk of the $NPPh_3^-$ ligand.

$[Nb(\eta^5\text{-}C_5H_5)Cl_4]$, prepared as described in literature from $NbCl_5$ and $Sn(C_5H_5)Bu^n_3$ in dichloromethane,[5] reacts with $Li(NRNR_2)$ in THF yielding diamagnetic $[Nb(\eta^5\text{-}C_5H_5)Cl_3(NRNR_2)]$ ($NRNR_2 = NMeNMe_2$ or $NPhNH_2$). $[Nb(\eta^5\text{-}C_5H_5)Cl_3(NMeNMe_2)]$ is stable in solution, as inferred from its NMR spectrum. However, $[Nb(C_5H_5)Cl_3(NPhNH_2)]$ behaves in a different way, and seems to lose the cyclopentadienyl ligand on standing in THF solution at room temperature.

We also have studied the reactions of $[V(C_5H_5)Cl_3]$ with phosphines and diphosphines. The complexes $[V(C_5H_5)Cl_3(\text{diphos})]$ (diphos = dppe or dmpe) can be prepared in high yields from $[V(C_5H_5)Cl_3]$ and the diphosphine in ether. However, the reaction with PMe_3 is accompanied by decomposition. Presumably reduction of vanadium(IV) to lower oxidation states occurs, and no stable adduct is isolated. The EPR spectra of the $[V(C_5H_5)Cl_3(\text{diphos})]$ complexes show well-defined eight-line patterns with lines broadened due to coupling with phosphorus.

The synthesis of new vanadium and niobium dinitrogen complexes was pursued. Reductions of $[V(C_5H_5)Cl_3]$ and $[Nb(C_5H_5)Cl_4]$ under different conditions yielded no dinitrogen complexes, but

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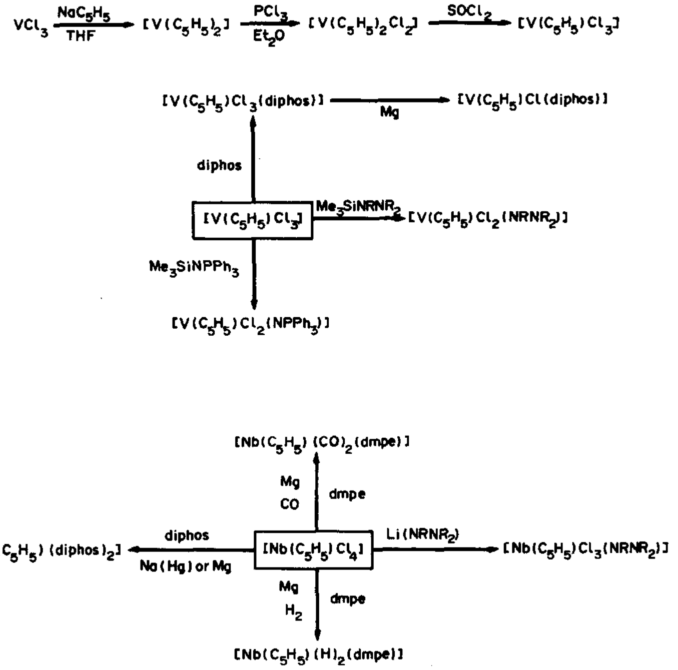

Scheme of reactions.

other low oxidation-state complexes of vanadium and niobium were readily isolated. For example, the reduction of [$V(C_5H_5)Cl_3$(dppe)] with Mg under N_2, leads to the complex [$V(C_5H_5)Cl$(dppe)].[6] [$Nb(C_5H_5)Cl_4$] is reduced either with Na(Hg) or Mg in the presence of a diphosphine yielding [$Nb(C_5H_5)$(diphos)$_2$]. The reduction of [$Nb(C_5H_5)Cl_4$] with Mg under CO in the presence of dmpe produces [$Nb(C_5H_5)(CO)_2$(dmpe)]. Reduction under H_2 affords red crystals analysing as [$Nb(C_5H_5)(H)_2$(dmpe)], which are not yet fully characterized.

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