DOCTORAL THESIS

Synthesis and chemistry of lanthanide complexes with phosphorus ylides, amides or porphyrinate ligands, and of transition metal complexes with polydentate ligands

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Synthesis and Chemistry of Lanthanide Complexes with Phosphorus Ylides, Amides or Porphyrinate Ligands, and of Transition Metal Complexes with Polydentate Ligands

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Abstract

The chemistry of organolanthanide phosphorus ylide complexes as a function of the size of lanthanide metals and the nature of the auxiliary ligands has been studied. The interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2LnCl{\cdot}LiCl]$ (Ln = Yb, Sm) and $Ln(NPh_2)_2Cl$ (Ln = Yb, Er) with the ylidic ligand $Li[(CH_2)(CH_2)PPh_2]$ gave compounds **I-1**~**I-5**, in which **I-4** and **I-5** are the very first structurally characterized anionic lanthanide-amide *ate* complexes that comprise a discrete cation and a homoleptic tetra-coordinated lanthanide-amide anion.

A new and convenient synthetic route for the preparation of cationic lanthanide (III) monoporphyrinate complexes has been developed. Reactions of an excess of $Ln[N(SiMe_3)_2]_3{\cdot}x[LiCl(THF)_3]$, generated *in situ* from the reaction of anhydrous $LnCl_3$ with 3 equivalents of $Li[N(SiMe_3)_2]$ in tetrahydrofuran, with 5, 10, 15, 20-tetrakis(*p*-methoxyphenyl)porphyrin (H_2TMPP) in refluxing tetrahydrofuran-bis(2-methoxyethyl) ether solution (1:6 v/v) gave the cationic monoporphyrinate complexes $[Ln^{III}(TMPP)(H_2O)_3]Cl$ (Ln = Yb **II-1**, Er **II-2**, or Y **II-3**), with 5, 10, 15, 20-tetrakis(*p*-tolyl)-porphyrin (H_2TTP) gave $[Yb^{III}(TTP)(H_2O)_2(THF)]Cl$ **II-4**, and with 5, 10, 15 ,20-tetrakis[(1*S*, 4*R*, 5*R*, 8*S*)-1, 2, 3, 4, 5, 6, 7, 8-octahydro-1,4:5,8-dimethano-anthracen-9-yl]-porphyrin D_4-symmetric porphyrin (H_2P*) gave $[Yb^{III}(P^*)(H_2O)_2(EtOH)]Cl$ **II-5**. The structures of compounds **II-1**~**II-5** have been established by X-ray crystallography. Metathesis of **II-1** with an excess of $AgBF_4$ gave the unexpected neutral monoporphyrinate complex $[Ag^{II}(TMPP)]$ **II-6** whose

structure was also determined. Compound **II-1** was found to catalyze the cyclotrimerization of phenyl isocyanate.

In addition, the interaction of H_2TTP and H_2TPP with an excess of $Y^{III}[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)]_3$ in refluxing bis(2-methoxyethyl) ether gave the neutral monoporphyrinate complexes $\{Y^{III}(TTP)[(CH_3OCH_2CH_2)_2O]\}$ **II-7** and $[Y^{III}(TPP)(Cl)(H_2O)(THF)]$ **II-8**, respectively. The interaction of H_2TMPP, H_2TTP and H_2TPP with an excess of $Yb^{III}(NPh_2)_3 \cdot x[LiCl(THF)_3]$, generate *in situ*, in refluxing bis(2-methoxyethyl) ether gave the neutral hydroxyl-bridged dinuclear porphyrinate complexes $[Yb^{III}(TMPP)(\mu\text{-}OH)]_2$ **II-9** and $[Yb^{III}(TTP)]_2(\mu\text{-}OH)(\mu\text{-}OCH_2CH_2OCH_3)$ **II-10**, and the neutral monoporphyrinate complex $[Yb(TPP)(Cl)(H_2O)(THF)]$ **II-11**, respectively. When an excess of $Yb^{III}[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)]_3$ was reacted with H_2TPP, work up in air gave an unexpected complex $[(TPP)Yb^{III}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2CCO_2)$ **II-12**. The structures of these six complexes have been established by X-ray crystallography.

Moreover, we studied the coordination behavior of polydentate ligands towards transition metals. Reaction of 3 equivalents of *o*-$Ph_2PC_6H_4(CHO)$ with $[Cu(CH_3CN)_4](ClO_4)$ and $AgBF_4$, gave $\{Cu[o\text{-}Ph_2PC_6H_4(CHO)]_3\}(ClO_4)$ **III-1** and $\{Ag[o\text{-}Ph_2PC_6H_4(CHO)]_3\}(BF_4)$ **III-2**, respectively. Reaction of 2 equivalents of *o*-$Ph_2PC_6H_4(CHO)$ with $PdCl_2(PhCN)_2$ gave *trans*-$[o\text{-}Ph_2PC_6H_4(CHO)]_2PdCl_2$ **III-3**. Reaction of **III-1** and **III-2** with 1,3-diaminopropane gave M(propyl-P_2N_2)(ClO_4) (M = Cu, **III-4** and Ag, **III-5**). The template condensation of $Ag(SO_3CF_3)$, $N(CH_2CH_2NH_2)_3$ and *o*-$Ph_2PC_6H_4(CHO)$ in 3:2:6 molar ratio in ethanol gave the

complex $(Ag_3L_2)(CF_3SO_3)_3$ {L = $[(o\text{-}Ph_2PC_6H_4)CH{=}NCH_2CH_2]_3N$}, **III-6**, and that of $NiCl_2{\cdot}6H_2O$, $N(CH_2CH_2NH_2)_3$ and $o\text{-}Ph_2PC_6H_4(CHO)$ in 1:1:3 molar ratio in ethanol gave the octahedral complex $\{NiCl[(H_2NCH_2CH_2)_2NCH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}PPh_2]\}(BF_4)$ **III-7**. While the reaction of $Ag(SO_3CF_3)$ with $N(CH_2CH_2NH_2)_3$, $o\text{-}Ph_2PC_6H_4(COOH)$ and 1,3-dicyclohexylcarbodiimide (DCC) in 1:1:3:3 molar ratio in ethanol gave $\{Ag(H_2NCH_2CH_2)_2NCH_2CH_2NHOC(Ph_2P\text{-}o\text{-}C_6H_4)\}CF_3SO_3$ **III-8.** The treatment of $Ag(SO_3CF_3)$, $N(CH_2CH_2NH_2)_3$ with $o\text{-}Ph_2PC_6H_4(COOH)$ in 1:1:1 molar ratio in ethanol gave $Ag_6[o\text{-}Ph_2P(C_6H_4COO)\text{-}O,P]_6$ **III-9**. All these complexes were characterized by X-ray crystallography.

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