The First Organolanthanide Complex of the Tripod Ligand $\{(\eta^8\text{C}_8\text{H}_8)\text{Sm}(\mu-\text{Cl})(\text{THF})\}_2$ ($\mathbf{1}$) with Na(\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}$ ($\mathbf{2}$) in a molar ratio of 1:2 in THF solution affords orange, crystalline $\{(\eta^8\text{C}_8\text{H}_8)\text{Sm}\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}$ ($\mathbf{3}$) as the first organolanthanide complex containing Kläui’s tripod ligand. The compound has been fully characterized by elemental analysis and spectroscopic methods.

**Keyword:** Lanthanides

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**Results and Discussion**

The organometallic tripod ligand $\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}$ was first reported by Werner et al. almost 30 years ago [2]. Since then it has been thoroughly investigated and shown to be a very versatile building block for the construction of various heterobimetallic complexes. The tridentate anion has been demonstrated by Kläui et al. to form stable coordination compounds with virtually all metal ions of the Periodic Table [3]. Coordination generally occurs via the oxygen atoms, and the ligand can be described as both weak and hard. Although derivatives of $\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}$ are organometallic compounds, they are chemically highly robust and are often stable towards air and even aqueous acids. Typical examples include neutral complexes formed with divalent metal ions such as $\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}_2\text{M}\$ (M = Mg, Ba, Zn, Mn). Trivalent lanthanide ions form cationic complexes of the type $\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}_2\text{M}^+$ (M = Ce, Pr, Nd, Eu, Gd, Ho, Tb) [4–6]. In the case of the 5f-elements, the uranium(IV) compound $\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}_2\text{UCl}_3(\text{THF})$ has been prepared and structurally characterized [7].

Although the cationic lanthanide derivatives are among the oldest known complexes of Kläui’s tripod ligand, quite surprisingly no organolanthanide compound containing this ligand has been reported so far [8]. It might be anticipated, that a combination of $\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}_2\text{Cl}$ with typical bent metallocene units such as (\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}_2\text{Sm}(\mu-\text{Cl})(\text{THF})\}_2$ ($\mathbf{1}$) with the yellow sodium salt Na(\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}$ ($\mathbf{2}$) in a molar ratio of 1:2 in THF solution according to Scheme 1 resulted in the formation of a deep red solution and precipitation of NaCl.

Extraction of the crude product with toluene followed by removal of insoluble materials and recrystallization from toluene/pentane afforded the novel samarium(III) “sandwich” complex $\{(\eta^8\text{C}_8\text{H}_8)\text{Sm}(\mu-\text{Cl})(\text{THF})\}_2$ ($\mathbf{1}$) + 2 Na(\{(\eta^5\text{C}_5\text{H}_5)\text{Co}\{\text{P(}\text{O})(\text{OEt})_2\}_3\}$ ($\mathbf{2}$) in the form of highly air-sensitive, orange crystals. The sensitivity of 3 towards oxygen is quite pronounced, despite the fact that the moleculealready contains three Sm-O bonds. The compound is soluble in toluene and THF, and melts without decomposition at 185 °C. The IR spectrum displays a sharp band at $\nu = 1144$ cm$^{-1}$, which can be assigned to the P=O valence vibration involved in a P-O-metal coordination [2].

**Scheme 1** Synthesis of 3.
The starting materials and decomposition points were determined on a chi 510 apparatus. Melting and charring points were recorded in a temperature range between 80 °C and −60 °C. The strongest temperature dependance was observed for those hydrogen atoms in closest proximity to the paramagnetic samarium atom, i.e., the cyclooctatetraenyl hydrogen atoms. Little or not influenced are the hydrogen atoms within the tripod ligand. A plot of the chemical shifts δ against the reciprocal temperature shows that the 1H NMR signals of 3 strictly follow the Curie Weiss law [10].

The with successful synthesis of the samarium compound 3 we have demonstrated that organolanthanide derivatives of the organometallic tripod ligand \([\text{C}_{2}H_{3}]\text{Co\{P(O)(OEt)_{2}\}}_{3}\) are accessible if the appropriate steric environment around the lanthanide atom is realized. In the “sandwich” complex 3 the large, flat cyclooctatetraenyl ligand provides sufficient steric protection of the large Sm(III) ion without causing any steric repulsion with the tripod ligand.

**Experimental**

**General Comments.** The reaction was carried out in an inert atmosphere of dry nitrogen using standard dry box and Schlenk techniques. IR spectra were recorded on a Bio-Rad FTS 7 spectrometer. NMR spectra were recorded on a Bruker AM 400 NMR spectrometer. Elemental analyses were performed at the Department of Inorganic Chemistry of the University of Göttingen. Melting and decomposition points were determined on an Büchi 510 apparatus. The starting materials 1 [11] and 2 [4] were synthesized according to literature procedures.

\(m/z\) 791 displaying the correct isotopic pattern. A peak at \(m/z\) 687 results from elimination of the cyclooctatetraenyl ligand.

The element combination cobalt/samarium is of special interest due to the great importance of samarium-cobalt magnets. Materials such as \(\text{SmCo}_{5}\) and \(\text{Sm}_{2}\text{Co}_{17}\) are among the strongest permanent magnets available and display a large energy product, coercive field strength and remanence combined with good thermal stability [9]. The paramagnetic shifts in the 1H NMR spectrum of 3 were studied in a temperature range between +80 °C and −60 °C. The strongest temperature dependance was observed for those hydrogen atoms in closest proximity to the paramagnetic samarium atom, i.e., the cyclooctatetraenyl hydrogen atoms. Little or not influenced are the hydrogen atoms within the tripod ligand. A plot of the chemical shifts δ against the reciprocal temperature shows that the 1H NMR signals of 3 strictly follow the Curie Weiss law [10].

With the successful synthesis of the samarium compound 3 we have demonstrated that organolanthanide derivatives of the organometallic tripod ligand \([\text{C}_{2}H_{3}]\text{Co\{P(O)(OEt)_{2}\}}_{3}\) are accessible if the appropriate steric environment around the lanthanide atom is realized. In the “sandwich” complex 3 the large, flat cyclooctatetraenyl ligand provides sufficient steric protection of the large Sm(III) ion without causing any steric repulsion with the tripod ligand.