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Telluroether Complexes of Platinum, Palladium, and Rhodium

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The preparation of a series of transition metal complexes containing $Te[CH_2Si(CH_3)_3]_2$ ligand is discussed. The complexes were characterized by X-ray crystallography and NMR spectroscopy.

Keywords Palladium; platinum; rhodium; telluroether; thioether

INTRODUCTION

The coordination chemistry of transition metal complexes containing chalcogeno ether ligands has seen rapid development over the past decades. It has been shown that $[MX_2(ERR')_2]$ (M=Pd, Pt; X=Cl, Br, I; E=Se, Te; R,R'=alkyl, aryl) can be present in solution as *cis*-and *trans*-isomers. The *trans/cis* ratio increases from platinum to palladium. In the solid-state platinum complexes can exist as both *trans*-and *cis*-isomers, while palladium complexes mostly show the presence of only *trans*-isomers. Information on complexes such as $[RhX_3(ERR')_3]$ is much sparser. It has been shown that octahedral mononuclear complexes containing three telluroether ligands may exist as *mer*- and *fac*-isomers in solution although in the solid-state only *mer*-isomers have been characterized. 4,5

In this contribution we discuss the synthesis and characterization of some Pt, Pd, and Rh complexes containing $Te[CH_2Si(CH_3)_3]_2^6$ ligands.

RESULTS AND DISCUSSION

The reaction of $Te[CH_2Si(CH_3)_3]_2$ with $[PtCl_2(NCPh)_2]$ leads to $[PtCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2].^7$ In solution, the ratio of \emph{cis} - and

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trans-isomers depends on the initial molar ratio of the reagents. With excess of $[PtCl_2(NCPh)_2]$ only cis-isomer is formed and with excess of $Te[CH_2Si(CH_3)_3]_2$ the main product is the transisomer. With metal-to-ligand molar ratio $1:1^1/_2$ and 1:2 a few crystals of $[Pt_2Cl_4(\mu-\{Te[CH_2Si(CH_3)_3]_2\})\{Te[CH_2Si(CH_3)_3]_2\}_2]$ was also obtained. The equimolar reaction of $[PdCl_2(NCPh)_2]$ with $Te[CH_2Si(CH_3)_3]_2$ affords $trans-[PdCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$ together with $[Pd_2(\mu-Cl)_2Cl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$. Stoichiometric amount or excess of $Te[CH_2Si(CH_3)_3]_2$ leads to good yields of mononuclear $trans-[PdCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$.

Reaction of equimolar amounts of $Te[CH_2Si(CH_3)_3]_2$ with $[MCl_2(SMePh)_2]$ (M = Pt, Pd) yields a mixture of complexes. In case of Pt, the ^{125}Te -NMR spectrum shows the signals of cis- and trans- $[PtCl_2\{Te[CH_2Si(CH_3)_3]_2\}(SMePh)]$ together with those of cis- and trans- $[PtCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$ (Figure 1). In case of Pd, the ^{125}Te -NMR spectrum indicates the formation of trans- $[PdCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$ (CH₃)₃]₂(SMePh)] and trans- $[PdCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$.

A mixture of complexes is also formed upon refluxing RhCl₃x3H₂O and Te[CH₂Si(CH₃)₃]₂ $(1:1^1/_2)$ in EtOH.⁸ Crystals of [Rh₂(μ -Cl)₂Cl₄(OHCH₂CH₃){Te[CH₂Si(CH₃)₃]₂}₃] were isolated from the mixture and characterized by X-ray crystallography. With molar ratio of $1:2^1/_2$, a mixture of [Rh₂(μ -Cl)₂Cl₄{Te[CH₂Si(CH₃)]₂}₄] and *mer*-[RhCl₃{Te[CH₂Si(CH₃)₃]₂}₃] is formed. Only *mer*-[RhCl₃{Te[CH₂-Si(CH₃)₃]₂}₃] is observed with the molar ratio of $1:3^1/_2$.

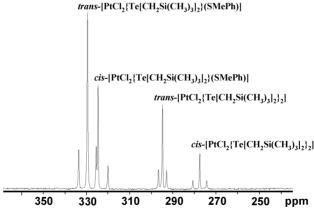
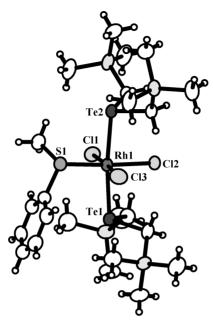
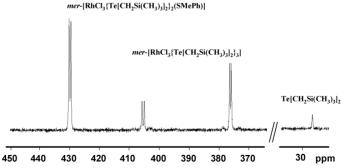


FIGURE 1 125 Te-NMR spectrum of the mixture containing cis- and trans-[PtCl₂{Te[CH₂Si(CH₃)₃]₂}(SMePh)] and cis- and trans-[PtCl₂{Te[CH₂Si-(CH₃)₃]₂}₂].



 $\textbf{FIGURE 2} \ \ The \ molecular \ structure \ of \ [RhCl_3\{Te[CH_2Si(CH_3)_3]_2\}_2(SMePh)].^8$

Two-to-one reaction of $Te[CH_2Si(CH_3)_3]_2$ with $[RhCl_3(SMePh)_3]$ results in a mixture of mer- $[RhCl_3(SMePh)_3]$, mer- $[RhCl_3\{Te[CH_2Si(CH_3)_3]_2\}_2(SMePh)]$ (see Figure 2), and mer- $[RhCl_3\{Te[CH_2Si(CH_3)_3]_2\}_3]$. The ^{125}Te resonance of uncoordinated $Te[CH_2Si(CH_3)_3]_2$ can still be seen in the NMR spectrum (Figure 3).



 $\label{eq:FIGURE} \textbf{FIGURE} \quad \textbf{3} \quad ^{125}\text{Te-NMR} \quad \text{spectrum} \quad \text{of} \quad \text{the} \quad \text{two-to-one} \quad \text{reaction} \quad \text{of} \quad \text{Te}[CH_2Si(CH_3)_3]_2 \quad \text{with} \quad [RhCl_3(SMePh)_3].$

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