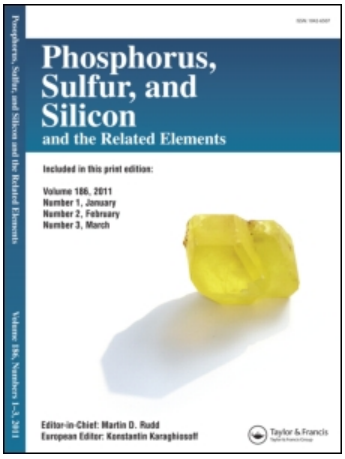

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Telluroether Complexes of Platinum, Palladium, and Rhodium

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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.[1] 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.[1–3] 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 *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 trans-isomer. With metal-to-ligand molar ratio $1:1^1/_2$ and 1:2 a few crystals of $[Pt_2Cl_4(\mu\text{-}\{Te[CH_2Si(CH_3)_3]_2\})\{Te[CH_2Si(CH_3)_3]_2\}_2]$ 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 $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$. 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*-$[PdCl_2\{Te[CH_2Si(CH_3)_3]_2\}(SMePh)]$ and *trans*-$[PdCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$.

A mixture of complexes is also formed upon refluxing $RhCl_3x3H_2O$ and $Te[CH_2Si(CH_3)_3]_2$ $(1:1^1/_2)$ in EtOH.[8] Crystals of $[Rh_2(\mu\text{-}Cl)_2Cl_4(OHCH_2CH_3)\{Te[CH_2Si(CH_3)_3]_2\}_3]$ were isolated from the mixture and characterized by X-ray crystallography. With molar ratio of $1:2^1/_2$, a mixture of $[Rh_2(\mu\text{-}Cl)_2Cl_4\{Te[CH_2Si(CH_3)]_2\}_4]$ and *mer*-$[RhCl_3\{Te[CH_2Si(CH_3)_3]_2\}_3]$ is formed. Only *mer*-$[RhCl_3\{Te[CH_2Si(CH_3)_3]_2\}_3]$ is observed with the molar ratio of $1:3^1/_2$.

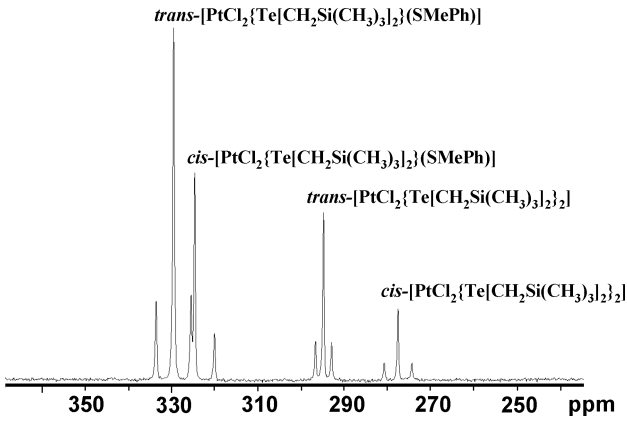

FIGURE 1 ^{125}Te-NMR spectrum of the mixture containing *cis*- and *trans*-$[PtCl_2\{Te[CH_2Si(CH_3)_3]_2\}(SMePh)]$ and *cis*- and *trans*-$[PtCl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$.

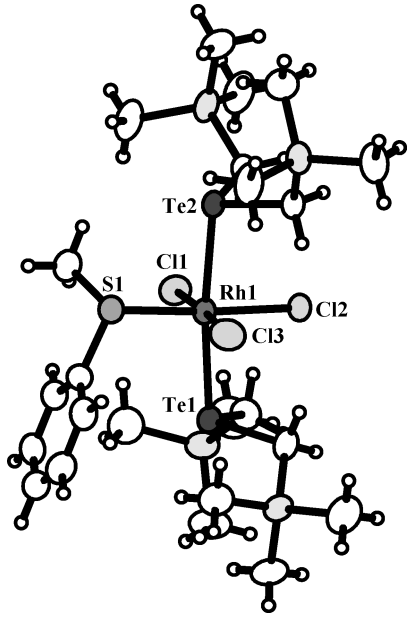

FIGURE 2 The molecular structure of $[RhCl_3\{Te[CH_2Si(CH_3)_3]_2\}_2(SMePh)]$.[8]

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).

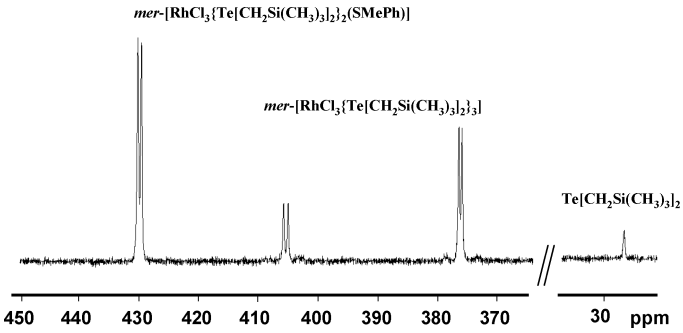

FIGURE 3 ^{125}Te-NMR spectrum of the two-to-one reaction of $Te[CH_2Si(CH_3)_3]_2$ with $[RhCl_3(SMePh)_3]$.

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