

Surprising Insights in the Various Molecular Structures of Hypercoordinate Bis(oxinato)silicon Complexes

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The syntheses of two cyclic diorganosilicon enamines $\text{RPhSi}(\overbrace{o-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{NCH}_2\text{Ph})=\text{CH}_2})_2$ [$\text{R} = \text{Ph}$ (**2a**), Me (**2b**)] are described. These compounds react with 8-oxyquinoline leading to bis(oxinato)silicon complexes $\text{RPhSi}(\text{oxinate})_2$ [$\text{R} = \text{Ph}$ (**5a**), Me (**5b**)]. Their X-ray structures reveal hexacoordination of the Si atom with the monodentate substituents in *cis*-positions and N atoms as well as O atoms in *trans*-positions.

In crystalline dimethylbis(oxinato)silicon, $\text{Me}_2\text{Si}(\text{oxinate})_2$ (**7**), the silicon atom is only bicapped tetrahedrally coordinated, while for dichlorobis(oxinato)silicon, $\text{Cl}_2\text{Si}(\text{oxinate})_2$ (**8**), there is an octahedral coordination of the Si atom with chlorine atoms in *trans*-positions. This conclusion is based on the results of spectroscopic analysis (IR, ^{29}Si CP/MAS NMR) as well as quantum chemical calculations. The first example of a silicon-bis-oxinate with the $\text{N} \rightarrow \text{Si}$ dative bonds in a *trans*-arrangement has been detected in the hexacoordinate silicon tris-chelate $(\text{oxinate})_2\text{Si}(\text{PhN}-\text{CH}_2\text{CH}_2-\text{NPh})$ (**11**). Its configuration was proven by X-ray structure analysis. Thus, for hexacoordinate bis(oxinato)silicon compounds three new architectures were found which complement the previously established building pattern of the N, N' -*cis*-O, O'-*trans*-bis(oxinato)silicon complexes.

The *mer*-tris(oxinato)siliconium cation (**9**⁺) (its configuration being proven by ^1H and ^{13}C NMR spectroscopy) features at least three coordination patterns with (O,O;N,N)-*cis*, *cis*-, -*cis*, *trans*- as well as -*trans*, *cis*-arrangements of two oxinate ligands.

Key words: Enamine, Hypercoordination, Oxinate, Silicon