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Complexes of Rhenium with Sterically Hindered Thiolate Ligands. Crystal Structure of $[Re(SC_6H_4\text{-}o\text{-}SiMe_3)\{NC(SC_6H_4\text{-}o\text{-}SiMe_3)CH_3\}_2(PPh_3)_2]$, a Complex Exhibiting Coordinated Thiolimidate Groups Formed via Nucleophilic Attack and Reduction by Thiolate of Coordinated Acetonitrile

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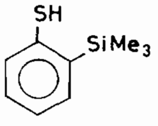
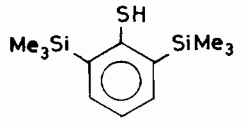
We have recently described the synthesis and coordination properties of a novel series of sterically hindered thiolate ligands, of which **I** and **II** are prototypes [1–3]. Since rhenium has been shown by one of us to possess a diverse chemistry with the



I



II

related ligand 2,4,6-triisopropylthiophenol (TIPTH) [4–7], the chemistry of **I** with various rhenium precursors was investigated. The structural prototype for rhenium thiolate structural chemistry is $[ReO(SR)_4]^-$ [8], which displays a square-pyramidal geometry with sterically innocent thiolates [9] and most hindered thiolates, such as TIPT [5], but exhibits some distortion toward trigonal bipyramidal in the specific case of 2,4,6-trimethylthiophenolate. The complex $(Ph_4P)[ReO(SC_6H_4\text{-}o\text{-}SiMe_3)_4]\cdot CH_2Cl_2$ (**III**) was synthesized and structurally characterized as a monitor of the gross influence of the steric bulk of the ligand. We further sought to examine the ability of the ligand to stabilize lower oxidation states of the metal and to incorporate organic substrate ligands into the $[Re(SR)_n]$ core by reacting $[ReCl_3(PPh_3)_2(CH_3CN)]$ with **I**. The complex $[Re(SC_6H_4\text{-}o\text{-}SiMe_3)\{NC(SC_6H_4\text{-}o\text{-}SiMe_3)CH_3\}_2(PPh_3)_2]$ (**IV**) is the unexpected product of this reaction.

Addition of an excess of **I** to a methanolic suspension of K_2ReCl_6, followed by addition of $(PPh_4)Br$, resulted in dark purple crystals of **III**. The infrared spectrum of **III** is characterized by features at 950 cm^{-1} and 840–860 cm^{-1}, attributed to $\nu(Re{=}O)$ and $\nu(Si{-}C)$, respectively. The structure of **III** is illustrated in Fig. 1, and selected bond lengths and angles are presented in the caption**. The structure of the anion consists of discrete mononuclear $[ReO(SC_6H_4\text{-}o\text{-}SiMe_3)_4]^{1-}$ anions which exhibit square-pyramidal geometry. The metrical parameters are unexceptional for a complex of this class and suggest that **I** does not impose steric requirements more severe than those associated with the TIPT ligand. The phenyl rings of the ligands are oriented nearly parallel to the Re–O vector, with the $-SiMe_3$ groups alternately *syn* and *anti* to the oxo group in order to minimize steric congestion.

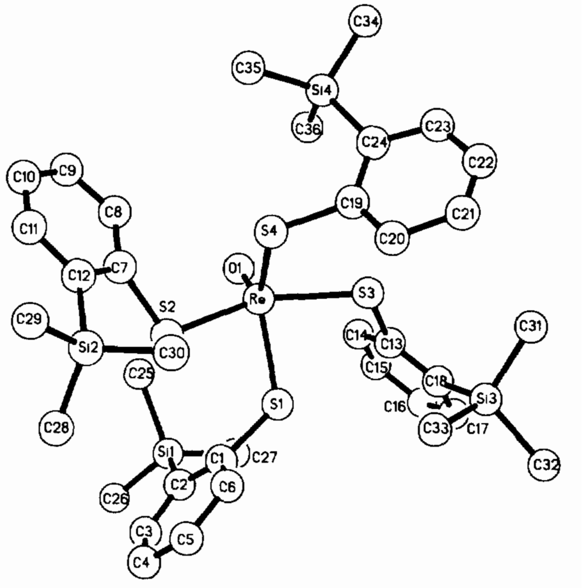


Fig. 1. ORTEP view of the structure of the molecular anion $[ReO(SC_6H_4\text{-}o\text{-}SiMe_3)_4]^{1-}$ of **III**. Selected bond lengths (Å) and angles (°): Re–S1, 2.369(5); Re–S2, 2.396(5); Re–S3, 2.377(5); Re–S4, 2.390(6); Re–O, 1.625(8); S2–Re–S3, 148.0(2); S1–Re–S4, 131.6(2); O1–Re–S1, 109.5(3); O1–Re–S2, 114.2(4); O1–Re–S3, 97.8(4); O1–Re–S4, 118.5(3).

Addition of a suspension of $[ReCl_3(PPh_3)_2(CH_3CN)]$ [10] in acetonitrile to an excess of **I** and triethylamine, followed by slow crystallization, produced Chinese red crystals of a complex analyzing for $[Re(SC_6H_4\text{-}o\text{-}SiMe_3)_3(PPh_3)_2(CH_3CN)_2]$. Bands attributable to coordinated CH_3CN were absent from the infrared spectrum, as was any indication of Re–oxo interactions. The most notable features were a band at 1630 cm^{-1}, assigned to $\nu(C{=}N)$ and the characteristic feature at 830–850 cm^{-1}, $\nu(Si{-}C)$.

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Crystal data for $(Ph_4P)[ReO(SC_6H_4\text{-}o\text{-}SiMe_3)_4]\cdot CH_2Cl_2$ (III**): monoclinic space group $P2_1/m$, a = 13.814(4) Å, b = 17.436(4) Å, c = 14.460(4) Å, β = 93.96(1)°, V = 3474.4(13) Å^3, D_{calc} = 1.29 g cm^{-3}. Structure solution and refinement based on 4637 reflections with $F_o > 6\sigma(F_o)$ (Mo Kα, λ = 0.71073 Å) converged at R = 0.0649.

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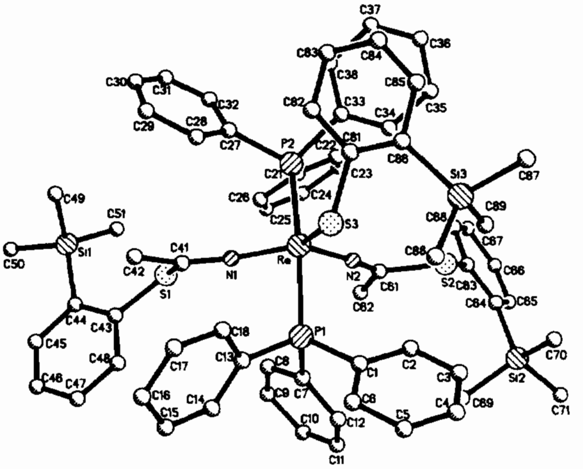

Fig. 2. ORTEP view of the structure of $[Re(SC_6H_4\text{-}o\text{-}SiMe_3)\{NC(SC_6H_4\text{-}o\text{-}SiMe_3)CH_3\}_2(PPh_3)_2]$ (IV), omitting the phenyl groups of the PPh_3 ligand. Selected bond lengths (Å) and angles (°): Re–S3, 2.323(2); Re–P1, 2.420(2); Re–P2, 2.424(2); Re–N1, 1.865(9); Re–N2, 1.867(8); N1–C41, 1.288(12); C41–S1, 1.804(11); C41–C42, 1.490(14); N2–C61, 1.266(11); C61–S2, 1.799(9); C61–C62, 1.503(12); P1–Re–P2, 169.6(1); N1–Re–N2, 126.2(3); N1–Re–S3, 119.6(3); N2–Re–S3, 113.4(2); Re–N1–C41, 178.5(7); Re–N2–C61, 170.3(7).

The structure of **IV** is shown in Fig. 2, with bond lengths and angles listed in the caption[†].

The Re center of **IV** assumes trigonal bipyramidal geometry with the phosphine donors occupying the axial positions and the equatorial plane defined by the thiolate sulfur S3 and nitrogen donors N1 and N2 of the thiolimidate ligands. The most unusual feature of the structure is the ligation of thiolimidate groups $[N{=}C(SC_6H_4\text{-}o\text{-}SiMe_3)CH_3]^-$ which are formed by nucleophilic attack on the coordinated nitrile by mercaptide and reduction of nitrile to the amido state. Although there is ample precedent for nucleophilic attack on coordinated nitriles [11–13] which tend to be electron deficient and for reduction of nitriles to amido groups [14], **IV** is a unique example of a structurally characterized complex exhibiting thiolimidate ligation. Since sterically innocent thiolates and conventional sterically hindered thiolates do not react with $[ReCl_3(PPh_3)(NCCH_3)]$ in this fashion, the unusual chemistry of **I** with coordinated nitrile may reflect the β-silicon effect of the substituent. We are currently investigating the reactions of **I** with other metal–nitrile complexes to determine whether thiolimidate formation is a general phenomenon with ligands of types **I** and **II**.

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[†] Crystal data for $[Re(SC_6H_4\text{-}o\text{-}SiMe_3)\{NC(SC_6H_4\text{-}o\text{-}SiMe_3)CH_3\}_2(PPh_3)_2]$ (IV): triclinic space group $P\bar{1}$, a = 13.351(2) Å, b = 14.969(3) Å, c = 17.611(4) Å, α = 86.45(1)°, β = 81.25(1)°, γ = 81.46(1)°, V = 3438.1(8) Å^3, Z = 2, D_{calc} = 1.29 g cm^{-3}; 6923 reflections, R = 0.0493.