

Notes

Synthesis of Unusual Rhenium Complexes with Schiff Bases

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Schiff bases offer a versatile and flexible series of ligands capable to bind with various metal ions to give complexes with suitable properties for theoretical and/or practical applications. Since Wilkinson published Schiff-base complexes in 1979,¹ a large number of polydentate Schiff-base compounds have been structurally characterized and extensively explored for the development of technetium and rhenium chemistry with radiopharmaceutical applications.² Research has been focused on the chemistry of (O,N,S)-tetradentate, at first, and later tridentate or bidentate Schiff-base complexes of Re and Tc.

Schiff bases generated by condensing 2-aminophenol with salicylaldehyde could act as a model of multidentate ligands towards rhenium and technetium cores.³ Especially, 2-(salicylideneamino)benzenethiol (SNO, *S*-phsalH₂) is not the stable form of this noncoordinated molecule, while 2-(2-hydroxyphenyl)phenol (ONO, *O*-phsalH₂) is stable.¹ At room temperature the *S*-phsalH₂ Schiff base converts to 2-(2-hydroxyphenyl)benzenethiazoline (hbtH) by an intramolecular ring closing reaction, which also converts to 2-(2-hydroxyphenyl)benzenethiazole (hbt) by an oxidative photochemical aromatization reaction as illustrated in Figure 1. Several oxometal complexes of *S*-phsalH₂/hbtH/hbt have extensively been studied.^{4,5} In the case of 2-(2-pyridyl)benzothiazoline, similar tautomerization of the ligand has been reported but only one tautomer exists in the solid state.^{4,5} However, attempt to isolate these Schiff base rhenium and technetium complexes with both of the tautomer *S*-phsalH₂/hbtH/hbt ligands have been unsuccessful. Here, we demonstrate reactions of these [SNO] and [ONO] Schiff

bases with Re(V) ions and interactions among the *S*-phsalH₂/hbtH/hbt ring tautomers. The crystal structures of the Re(O)(*S*-phsal)(hbt) and ReCl₂(*O*-phsal)(OPPh₃) are described, respectively.

The [SNO] complex [ReO(η³-*S*-phsal)(η²-hbt) (1) and the [ONO] complex [ReCl₂(OPPh₃)(η³-*O*-phsal)] (2) were obtained from reaction of [BzEt₃N](ReOCl₄) with *S*-phsalH₂ at room temperature and *t*-ReOCl₃(PPh₃)₂ with *O*-phsalH₂ on heating, respectively.⁶ These complexes were characterized by elemental analyses, spectroscopic methods and X-ray crystallography.⁷

The crystallographic analysis of 1 shows the presence of a neutral oxorhenium(V) complex in which the overall geometry around the central rhenium atom is best described as a distorted octahedron: the S, N and O atoms of the tridentate [SNO] ligand form in a *mer*-coordination, and the O and N atoms of the hbt ligand bind bidentately as depicted in Figure 2. The Re=O, Re-S, Re-O and Re-N bond lengths are in the ranges observed for analogous compounds. The Re-S(1) bond distance of 2.311(2) Å is longer than those of Re-O(1) (2.075(6) Å) and Re-N(1) (2.082(6) Å) on the equatorial plane, and that of Re-O(2) (1.963(6) Å) on the axial position, showing that the structural *trans* influence of the oxo group is not transmitted to oxygen atom. The most striking feature of the crystal structure of 1 is the bidentate binding of the hbt rather than the tridentate one of Hhbt. This is clearly seen from the formation of the thiazole: the difference of the distance between C(14) and N(2); 1.318(11) Å vs. 1.333(9) Å for C(1)-N(1) single bond of the *S*-phsal ligand. The C=N distances of hbt

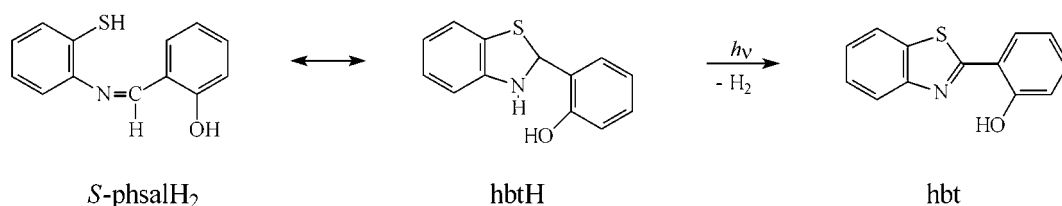


Figure 1. Schematic diagram of tautomerization between 2(2-hydroxyphenyl)benzenethiol (*S*-phsalH₂) and 2(2-hydroxyphenyl)benzenethiazoline (hbtH), and conversion to 2(2-hydroxyphenyl)benzenethiazole (hbt).

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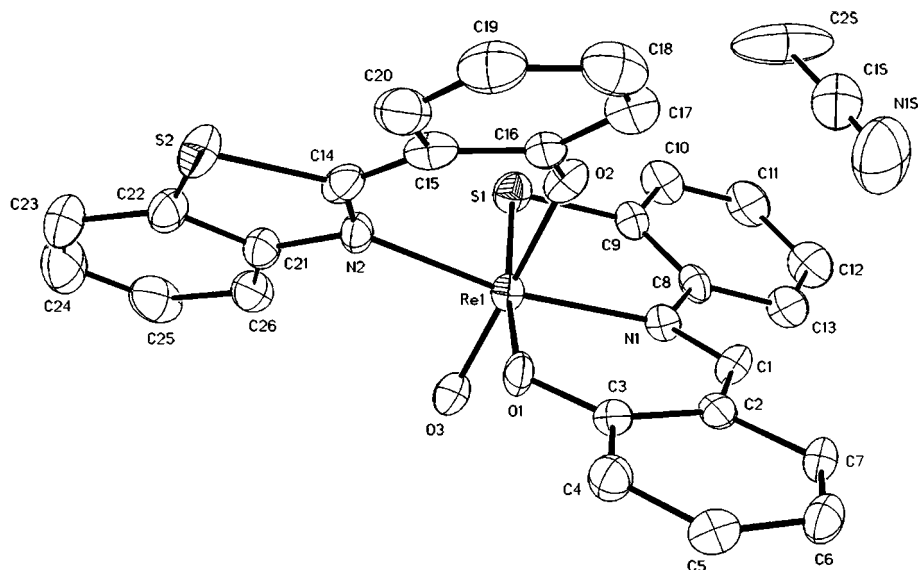


Figure 2. ORTEP drawing of $[\text{ReO}(\eta^3\text{-S-phsal})(\text{h}^2\text{-hbt})]$ (**1**). Selected bond lengths (Å) and angles ($^\circ$): Re(1)-O(1), 2.075(6); Re(1)-O(2), 1.963(6); Re(1)-O(3), 1.677(6); Re(1)-N(1), 2.082(6); Re(1)-N(2), 2.160(7); Re(1)-S(1), 2.311(2); N(1)-C(1), 1.333(9); N(2)-C(14), 1.318(11); N(1)-Re(1)-N(2), 166.7(3); O(1)-Re(1)-S(1), 170.56(17); O(2)-Re(1)-O(3), 166.8(2).

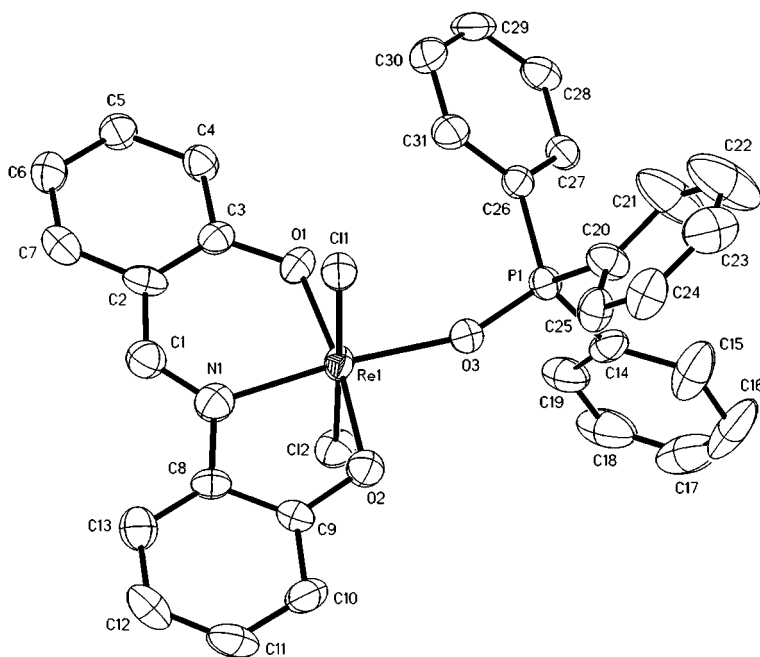


Figure 3. ORTEP drawing of $[\text{ReCl}_2(\text{OPPh}_3)(\eta^3\text{-O-phsal})]$ (**2**). Selected bond lengths (Å) and angles ($^\circ$): Re(1)-O(1), 1.957(3); Re(1)-O(2), 1.987(3); Re(1)-O(3), 2.027(3); Re(1)-N(1), 2.063(4); Re(1)-Cl(1), 2.3362(11); Re(1)-Cl(2), 2.3542(10); N(1)-C(1), 1.281(6); N(1)-Re(1)-O(3), 166.7(3); O(1)-Re(1)-O(2), 172.54(13); Cl(1)-Re(1)-Cl(2), 177.69(4).

have been reported: 1.332(10) Å for $[\text{TcOCl}_3(\text{hbt})]^-$.^{4b} The average angle around C(14) is 120.0(4) $^\circ$, that means sp^2 hybrid.

The X-ray structure of **2** is shown in Figure 3. The rhenium is six-coordinate in a distorted octahedral coordination sphere: the Cl_2 fragment is in *trans* arrangement and the O_3 fragment is in a *meridional* coordination. The O and N atoms of the *O*-phsal ligand bind tridentately, and the distance between C(1) and N(1) of the ligand is 1.281(6) Å, which means a C=N bond. The feature of this structure is

based on the formation of triphenylphosphine oxide, and therefore the oxidation state of the rhenium is +4. In most of reactions of trichlorobis(triphenylphosphine)oxorhenium (V), the rhenium-oxygen double bond is untouched and remains. Limited studies have been available regarding rhenium(IV) complexes with triphenylphosphine oxide.⁸ The nitrogen atom lies *trans* to OPPh_3 oxygen, and the value of 2.063(4) Å for the Re-N bond is found in the range 2.030(5)-2.091(6) Å for the other phosphine oxide Re complexes.^{8c} This structural *trans* effect is not so strong

compared to that of Re(III)-PPh₃ due to weak back-bonding ability of Re(IV) to OPPh₃.

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- The [SNO] complex [ReO(η^3 -S-phsal)(η^2 -hbt) (**1**) was prepared from addition of the mixture of [BzEt₃N](ReOCl₄) (0.20 g, 0.37 mmol) in 30 mL of chloroform and 3 mL of methanol to yellow solution of S-phsalI₂ (69 mg, 0.30 mmol) in 10 mL of chloroform at room temperature. After recrystallization of the crude from acetonitrile, brown crystals of complex **1** were obtained with 80% yield based on rhenium. On the other hand, a solution of *t*-ReOCl₃(PPh₃)₂ (200 mg, 0.24 mmol) and *O*-phsalH₂ (56 mg, 0.26 mmol) in 50 mL of CH₂Cl₂ was refluxed for 1 h, and the solvent of the resulting red mixture was removed to red-brown powder. After recrystallization of the powder from CH₂Cl₂ and hexane, the [ONO] complex [ReCl₂(OPPh₃)(η^3 -*O*-phsal)] (**2**) was obtained in 80% yield.
- Brown plate crystals of **1** were analyzed at 273 ± 1 K: orthorhombic, space group *Pbca* with *a* = 13.1266(8) Å, *b* = 16.6892(10) Å, *c* = 23.4392(14) Å, *a* = 90°, *b* = 90°, *g* = 90°, *V* = 5134.9(5) Å³, *Z* = 8, *d*_{calc} = 1.803 g/cm³, μ_r (Mo K α) = 4.932 mm⁻¹, goodness of fit on *F*² = 0.887, *R* = 0.0510 and *R*_w = 0.1262. ¹H-NMR in DMSO-*d*₆: δ 6.2 (m, 1H, ph), 6.3 (m, 1H, ph), 6.6 (m, 1H, ph), 7.0 (m, 1H, ph), 7.1-7.4 (m, 5H, ph), 7.6-7.9 (m, 5H, ph), 8.4 (m, 1H, ph), 8.6 (m, 1H, ph) and 9.7 (m, 1H, -CH-N-). FT-IR (KBr pellet, cm⁻¹): 955 (Re-O), 1608 (C-N). Anal. Calcd. for C₂₈H₂₀N₃O₃ReS₂: C, 48.26; H, 2.89; N, 6.03%. Found: C, 48.20; H, 3.01; N, 5.85%. Brown plate crystals of **2** were analyzed at 158 ± 1 K: monoclinic, space group *P2(1)* with *a* = 13.9609(6) Å, *b* = 14.6346(6) Å, *c* = 14.4209(6) Å, α = 90°, *b* = 108.1490(10)°, γ = 90°, *V* = 2799.8(2) Å³, *Z* = 4, *d*_{calc} = 1.771 g/cm³, μ_r (Mo K α) = 4.622 mm⁻¹, goodness of fit on *F*² = 1.021, *R* = 0.0310 and *R*_w = 0.0799. ¹H-NMR in DMSO-*d*₆: δ 6.9 (m, 4H, ph), 7.3 (m, 4H, ph), 7.5 (m, 15H, PPh₃), and 10.2 (s, 1H, -CH-N-). FT-IR (KBr pellet, cm⁻¹): 1597 (C-N). Anal. Calcd. for C₃₁H₂₄Cl₂NO₃PRE: C, 49.87; H, 3.24; N, 1.88%. Found: C, 50.07; H, 3.49; N, 1.93%. Crystallographic details and complete listings of **1** and **2** have been deposited at the Cambridge Crystallographic Data Center (Deposition No. CCDC-197630 and CCDC-197631), respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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