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Syntheses and structural characterization of rhenium-bis-hydrazinopyrimidine core complexes with thiolate and Schiff base coligands

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Abstract

The reaction of perrhenate with 2-hydrazinopyrimidine in MeOH–HCl yields $[\text{ReCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**1**). The analogous reaction with Na_2MoO_4 yields $[\text{MoCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNHC}_4\text{H}_3\text{N}_2)]$ (**1a**). The reaction of **1** with pyrimidine-2-thiol and triethylamine produces $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**), while reaction of **1** with the Schiff base $\text{HSC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{OH}$ provides $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ (**4**), was also synthesized by reacting $[\text{ReCl}_3(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ with $\text{HSC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{OH}$. The crystal structures of **1–4** have been determined.

Keywords

Rhenium-hydrazinopyrimidine compounds; Rhenium-Schiff base compounds; Radiopharmaceuticals; X-ray structures

1. Introduction

The contemporary development of technetium and rhenium coordination chemistry is driven by applications to nuclear medicine [1–7]. One approach to the design of diagnostic radiopharmaceuticals exploits 2-hydrazinonicotinamine as a bifunctional chelate for the labeling of derivatized peptides with $^{99\text{m}}\text{Tc}$ [8–10]. The modeling of the technetium-organohydrazine core of these radiopharmaceutical reagents has focused on the elaboration of a family of compounds derived from the technetium and/or rhenium bis-hydrazinopyridine core, $\{\text{Re}(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})\}^{3+}$ [11].

In an effort to expand this approach to the radio-labeling of proteins and peptides, we have begun to develop the parallel chemistry of hydrazinopyrimidine as the potential structural core for a bifunctional linker group [12]. While the chemistry of 2-hydrazinopyrimidine is often analogous to that of 2-hydrazinopyridine, it does offer some advantages in terms of solubility and derivatization. In an effort to develop the comparative chemistries of 2-hydrazinopyridine and 2-hydrazinopyrimidine with rhenium, the starting material $[\text{ReCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**1**) was prepared and reacted with mercaptopyrimidine and Schiff base compounds, both of which had previously been

demonstrated to act as useful coligands for the purification and stabilization of the radiopharmaceutical preparations [11,13]. The syntheses and structures of the rhenium-bis-pyrimidinodiazine core complexes $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**) and $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]\cdot 0.6\text{CH}_2\text{Cl}_2$ (**3**· $0.6\text{CH}_2\text{-Cl}_2$) are reported, as well as the analogous 2-pyridinodiazene core complex $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ (**4**).

2. Experimental

2.1. General considerations

NMR spectra were recorded on a Bruker DPX 300 (^1H 300.10 MHz) spectrometer in CD_2Cl_2 (δ 5.32). IR spectra were recorded as KBr discs with a Perkin–Elmer Series 1600 FTIR. Elemental analysis for carbon, hydrogen, and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. All reagents and solvents, apart from 2-hydrazinopyrimidine (Lancaster) were purchased from Aldrich Chemical Co. and used as received, unless otherwise stated. The $[n\text{-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4(\text{OPPh}_3)]$ [14] and *N*-(2-mercaptophenyl) salicylideneimine [15] were synthesized according to published procedures.

2.2. Syntheses

2.2.1. Preparation of $[\text{ReCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (1**)**—Into a 5 ml Schlenk flask was placed $[\text{NH}_4][\text{ReO}_4]$ (0.015 g, 0.056 mmol), 2-hydrazinopyrimidine (0.050 g, 0.450 mmol) and 2.0 ml of methanol. The reaction was stirred briefly and 0.01 ml of aqueous 36% HCl (0.30 mmol) was added dropwise. The reaction was heated to reflux for 20 min. The dark red solid was washed with 5 ml portions of MeOH and dried (0.0141 g, 49.5%). *Anal.* Calc. for $\text{C}_8\text{H}_8\text{N}_8\text{Cl}_3\text{Re}$: C, 18.9; H, 1.58; N, 22.0. Found: C, 18.9; H, 1.62; N, 21.5%. Compound **1** may also be prepared using $[n\text{-(C}_4\text{H}_9)_4\text{N}][\text{ReOBr}_4(\text{OPPh}_3)]$ as a starting material.

2.2.2. Preparation of $[\text{MoCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNHC}_4\text{H}_3\text{N}_2)]$ (1a**)**—A mixture of Na_2MoO_4 (0.050 g, 0.243 mmol), 2-hydrazinopyrimidine (0.147 g, 1.33 mmol) and 36% HCl (0.029 g, 0.794 mmol) in 6 ml of acetonitrile was placed in a glass tube. The contents were frozen in liquid nitrogen and the tube was flame sealed under vacuum to give a 32% fill volume. The tube was placed in an oven at 110°C for 3 days. Bright red crystals were allowed to air-dry to give 0.052 g of **1a** (yield: 51%). IR (KBr pellet, cm^{-1}): 3022 (m), 1618 (s), 1595 (s), 1555 (w), 1508 (m), 1452 (m), 1421 (s), 1368 (m), 1315 (m), 1277 (s), 1184 (m), 1156 (m), 996 (m), 870 (w), 754 (w), 616 (w), 490 (w). *Anal.* Calc. for $\text{C}_8\text{H}_9\text{N}_8\text{Cl}_3\text{Mo}$ (mol. wt. 419.52): C, 22.9; H, 2.16; N, 26.7. Found: C, 22.6; H, 2.35; N, 26.9%.

2.2.3. Preparation of $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{H}_2\text{S})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-NHNC}_4\text{H}_3\text{N}_2)]$ (2**)**—A solution of $[\text{ReCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{NNH})(\eta^2\text{-NHNC}_4\text{H}_3\text{N}_2)]$ (0.050 g, 0.0983 mmol) with pyrimidine-2-thiol (0.022 g, 0.196 mmol) and triethylamine (0.029 g, 0.287 mmol) in 10 ml of ethanol was stirred and refluxed overnight. The reaction mixture was filtered and the black precipitate was allowed to air-dry. Dark red crystals were grown by slow diffusion of pentane into a solution of the compound in methylene chloride (0.033 g, yield: 54%). IR (KBr pellet, cm^{-1}): 3450 (m), 1686 (w), 1622 (s), 1606 (s), 1550 (s), 1458 (m), 1421 (s), 1372 (s), 1294 (s), 1242 (m), 1225 (m), 1167 (m), 1148 (m), 1014 (w), 822 (m), 763 (m), 752 (m), 741 (w), 600 (w). *Anal.* Calc. for $\text{C}_{16}\text{H}_{13}\text{N}_{12}\text{S}_2\text{Re}$ (mol. wt. 623.70): C, 30.81; H, 2.10; N, 26.95. Found: C, 29.73; H, 2.31; N, 27.22%.

2.2.4. Preparation of $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{-C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-NHNC}_4\text{H}_3\text{N}_2)]\cdot 0.6\text{CH}_2\text{Cl}_2$ (3**· $0.6\text{CH}_2\text{Cl}_2$)**—A solution of $[\text{ReCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{NNH})(\eta^2\text{-$

NHNC₄-H₃N₂)] (0.050 g, 0.0983 mmol) with HSC₆H₄N=C(H)C₆H₄OH (0.068 g, 0.295 mmol) and triethylamine (0.059 g, 0.583 mmol) in 10 ml of ethanol was stirred and refluxed overnight. The reaction mixture was filtered and the dark red precipitate was allowed to air-dry. Dark red crystals were grown by slow diffusion of pentane into a methylene chloride solution of the solid yielding 0.033 g (yield: 49%). IR (KBr pellet, cm⁻¹): 1686 (w), 1605 (s), 1542 (s), 1459 (s), 1421 (s), 1294 (m), 1212 (m), 1146 (m), 1066 (m), 806 (w), 755 (m), 641 (w), 609 (w), 464 (w). *Anal.* Calc. for C_{21.60}H_{17.20}Cl_{1.20}N₉OSRe (mol. wt. 679.64): C, 38.17; H, 2.55; N, 18.55. Found: C, 38.34; H, 2.71; N, 18.09%.

2.2.5. Preparation of [Re(η³-SC₆H₄N=C(H)C₆H₄O)(η¹-NNC₅H₄N)(η²-NHNC₅H₄N)] (4)—A solution of [ReCl₃(η¹-NNC₅H₄NH)(η²-NHNC₅-H₄N)] (0.050 g, 0.0983 mmol) with HSC₆H₄N=C(H)C₆H₄OH (0.068 g, 0.295 mmol) and triethylamine (0.059 g, 0.583 mmol) in 10 ml of ethanol was stirred and refluxed overnight. The reaction mixture was filtered and the dark red precipitate was allowed to air-dry. Dark red crystals were grown by slow diffusion of pentane into a solution of the compound in methylene chloride (0.034 g, yield: 55%). ¹H NMR (CD₂Cl₂, ppm): 6.54 (m, 1H), 6.78–6.88 (mm, 3H), 7.06–7.20 (mm, 2H), 7.38–7.45 (mm, 2H), 7.51–7.72 (mm, 7H), 7.83 (m, 1H), 8.40 (m, 1H), 9.03 (s, 1H). IR (KBr pellet, cm⁻¹): 1684 (w), 1605 (s), 1542 (s), 1459 (s), 1423 (s), 1295 (m), 1210 (m), 1149 (m), 1063 (m), 807 (w) 758 (m), 641 (w), 609 (w), 464 (w). *Anal.* Calc. for C₂₃H₁₈N₇OSRe (mol. wt. 626.70): C, 44.08; H, 2.90; N, 15.64. Found: C, 44.45; H, 2.38; N, 16.01%.

2.3. X-ray crystallography

Data were collected on a Bruker SMART diffractometer system using graphite monochromated Mo Kα radiation (λ(Mo Kα)=0.71073 Å). Data collections were carried out at low temperature (85–94 K). The crystal parameters and other experimental details of the data collections are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the supplementary information. The structures were solved by direct methods [16]. Neutral atom scattering factors were taken from Cromer and Waber [17] and anomalous dispersion corrections were taken from those of Creagh and McAuley [18]. All calculations were performed using SHELXTL [16]. Non-hydrogen atoms were refined anisotropically. No anomalies were encountered in the refinements of any of the structures. Atomic positional parameters for the structures have been deposited with the Cambridge Structural Database.

3. Results and discussion

The parent rhenium-pyrimidinohydrazine compound [ReCl₃(η¹-NNC₄H₃N₂H)(η²-HNNC₄H₃N₂)] (**1**) was readily prepared in moderate yield in the reaction of perrhenate with 2-hydrazinopyrimidine in MeOH–HCl. As noted previously for the synthesis of the analogous hydrazinopyridine derivative [ReCl₃(η¹-NNC₅H₄NH)(η²-HNNC₅H₄N)] [11], the reaction involves the reduction of rhenium from Re(VII) to Re(III) with concomitant two-electron oxidation and two-proton elimination of each of the two hydrazinopyrimidine ligands, which consequently adopt neutral organodiazene or pyrimidinium-diazenido forms in the product.

Compound **1** is insoluble in most common organic solvents, except for DMF. However, attempts to recrystallize **1** from DMF–MeOH resulted in the isolation of the tetranuclear cluster [Re(η¹-NNC₄H₃N₂)(η²-HNNC₄H₃N₂)(OCH₃)₂]₄ [12]. In an attempt to provide a structurally characterized example of the metal-bispyrimidinohydrazine core, the red, diamagnetic complex [MoCl₃(η¹-NNC₄H₃N₂H)(η²-HNNHC₄H₃N₂)] (**1a**) was prepared. In a fashion similar to the Re analog, the molybdenum formally undergoes a four-electron

reduction from Mo(VI) in the molybdate precursor to Mo(II) in **1a**. Likewise, two hydrazinopyrimidine ligands each undergo two-electron oxidation. However, one of these exhibits a single proton elimination to adopt the cationic pyrimidinohydrazinium form.

Compound **1** reacts with a variety of coligands with facile substitutions of the chloride sites. Thus, the reaction of **1** with 2-mercaptopyrimidine yields $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^1\text{-NNC}_4\text{H}_3\text{N}^2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**), as a consequence of displacement of three chlorides from the parent **1** and deprotonation of the pyrimidinium-diazenido ligand to give the pyrimidinohydrazido(1[−]) form of the ligand.

Similarly, the reaction of **1** with the Schiff base *N*-(2-mercaptophenyl)salicylideneimine proceeds smoothly to the product $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^1\text{-HNNC}_4\text{H}_3\text{N}_2) \cdot 0.6\text{CH}_2\text{Cl}_2]$ (**3**·0.6·CH₂Cl₂).

Compounds **1–4** all exhibit a strong band in the IR spectra in the range 1550–1595 cm^{−1} assigned to ν(N=N), suggesting that these compounds exhibit comparable ligand multiple bonding character despite variations in metal and organohydrazine type. The IR spectra of **3** and **4** also exhibit a strong band at 1605 cm^{−1}, characteristic of ν(C=N) for the Schiff base (Scheme 1).

The ¹H NMR spectra of the compounds are unexceptional, with the exception of the spectra of **3** and **4** which exhibit a singlet at 9.07 and 9.03 ppm, respectively, integrating for a single proton and assigned to the imine proton of the Schiff base, in agreement with previous reports [15].

As shown in Fig. 1, $[\text{MoCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNHC}_4\text{H}_3\text{N}_2)]$ (**1a**) exhibits distorted octahedral geometry, defined by three chloride ligands, the α-nitrogen of a monodentate pyrimidinium-diazenido ligand and the α-nitrogen and a pyrimidine nitrogen of the cationic pyrimidinohydrazinium ligand. The chloride donors adopt a meridional orientation; consequently, the remaining meridional positions are defined by the three nitrogen donors.

The geometry of the $\{\text{Mo}(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNHC}_4\text{H}_3\text{N}_2)\}^{3+}$ core of **1b** is similar to that previously reported for the hydrazinopyridine analogs $[\text{MoCl}_3(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNHC}_5\text{H}_4\text{N})]$ and $[\text{ReCl}_3(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$, with a coplanar arrangement of the entire metal-bisorganohydrazino unit. The metrical parameters for the pyrimidinium-diazenido group, $\{\text{NNC}_4\text{H}_3\text{N}_2\text{H}\}$, and the pyrimidinehydrazinium unit, $\{\text{HNNHC}_4\text{H}_3\text{N}_2\}^+$, of **1a** are similar to those observed for $[\text{MoCl}_3(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNHC}_5\text{H}_4\text{N})]$. The geometry of the $\{\text{Mo}(\eta^2\text{-HNNHC}_5\text{H}_4\text{N})\}^{3+}$ chelate ring is also similar to the $\{\text{Re}(\text{HNNHR})\}^{n+}$ ring moieties of $[(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2\{\text{HNN}(\text{CH}_3)\text{C}_6\text{H}_4\text{Me}\}][\text{BF}_4]$ [19], $[\text{ReO}\{\text{HNNC}(\text{S})\text{Ph}\}\{\text{HNNHC}(\text{S})\text{Ph}\}]$ [20], and $[\text{Re}\{\text{HNNC}(\text{S})\text{Ph}\}-\{\text{HNNHC}(\text{S})\text{Ph}\}_2][\text{Cl}]$ [21], as summarized in Tables 2–6.

The nitrogen-bound protons of **1a** were clearly distinguishable on the electron density maps, and the locations are consistent with those from previously determined structures. The degree of protonation is also consistent with charge-balance considerations and with the observed diamagnetism of **1a**. The Mo–N(5) bond distance of 1.741(3) Å, the N(5)–N(6) bond distance of 1.301(4) Å and the Mo–N(5)–N(6) bond angle of 174.4(3)° are consistent with considerable multiple bond delocalization throughout the $\{\text{Mo–N(5)–N(6)}\}$ unit. The Mo–N(1) bond distance of 1.939(4) Å is slightly shorter than a typical single bond

due to some delocalization of the π system of the ligand. In comparing the structures of **1b** and $[\text{MoCl}_3(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNHC}_5\text{H}_4\text{N})]$ to that of $[\text{ReCl}_3(\eta^1\text{-NNC}_5\text{H}_4\text{NH})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$, the major geometric consequence of protonation of the β -nitrogen position is a lengthening of N–N bond distance from 1.308 Å in the $\{\text{Re}(\text{HNNR})\}$ unit to approximately 1.365 Å in the $\{\text{Mo}(\text{HNNHR})\}$ moiety.

The structure of the mercaptopuridine derivative $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**) is shown in Fig. 2. The chloride ligands of **1** have been replaced by the sulfur donor of a monodentate mercaptide ligand and the sulfur and nitrogen donors of a chelating mercaptopuridine ligand. The $\{-\text{NNC}_4\text{H}_3\text{NH}\}$ diazene ligand of **1** has been deprotonated to the mononegative diazenido(–1) form. The diazene form of the chelating ligand has been retained, with protonation at the N(5) or α -nitrogen site. The planar orientation of the $\{\text{Re}(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N})\}^{3+}$ core has been maintained. The thiolate sulfur donors adopt a *trans* orientation. The structure of **3** is essentially identical to that previously reported for the pyridine analog $[\text{Re}(\eta^1\text{-SC}_5\text{H}_4\text{N})(\eta^2\text{-SC}_5\text{H}_4\text{N})(\eta^1\text{-NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ [11].

The structure of the Schiff base derivative $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**3**) is shown in Fig. 3. The distorted octahedral geometry is defined by the nitrogen donors of the chelating and terminal pyrimidinohydrazino ligands and the O, S and N donors of the tridentate Schiff base ligand. The geometry of the $\{\text{Re}(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N})\}^+$ core of **3** is similar to that observed for **2**. The metrical parameters involving the Schiff base donor are unexceptional. Curiously, the pyrimidine ring of the $\eta^1\text{-NNC}_4\text{H}_3\text{N}_2$ unit is no longer coplanar with the $\{\text{Re}(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)\}$ chelate plane, but has rotated to a nearly perpendicular orientation, a feature which contrasts with the structure of the pyridinohydrazine derivative $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ (**4**).

As shown in Fig. 4, the structure of **4** is similar to that of **3**, except for the retention of the planarity of the $\{\text{Re}(\eta^1\text{-NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})\}^{2+}$ core. The relative orientations of the organohydrazino rings of compounds with the $\{\text{M}(\eta^1\text{-NNR})(\eta^2\text{-NNR})\}^{n+}$ cores appear to reflect crystal packing influences or steric effects, as there are no consistent trends between degree of protonation or ligand metrical parameters and the planarity of the core.

4. Conclusions

The hydrazinopyrimidine chemistry of rhenium is readily accessed through a conveniently prepared precursor, $[\text{ReCl}_3(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**1**). Compound **1** reacts with a variety of ligands, such as thiols and Schiff bases, with substitution at the chloride positions and retention of the robust $\{\text{Re}(\eta^1\text{-NNR})(\eta^2\text{-NNR})\}^{n+}$ core. The representative derivatives $[\text{Re}(\eta^1\text{-SC}_4\text{H}_3\text{N}_2)(\eta^2\text{-SC}_4\text{H}_3\text{N}_2)(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**) and $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**3**) have been prepared and structurally characterized.

5. Supplementary material

Refer to Web version on PubMed Central for supplementary material.

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Scheme 1.

Fig. 1.
A view of the structure of **1a**, showing the atom-labeling scheme and 50% probability ellipsoids.

Fig. 2.
A view of the structure of **2**, showing the atom-labeling scheme and 50% probability ellipsoids.

Fig. 3.
A view of the structure of **3**, showing the atom-labeling scheme and 50% probability ellipsoids.

Fig. 4.
A view of the structure of **4**, showing the atom-labeling scheme and 50% probability ellipsoids.

Table 1

Summary of crystal data for the structural determinations of $[\text{MoCl}_3(\eta^1\text{NNC}_4\text{H}_3\text{N}_2\text{H})(\eta^2\text{-HNNHC}_4\text{H}_3\text{N}_2)]$ (**1**), $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^1\text{-NNc}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**), $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)] \cdot 0.6\text{CH}_2\text{Cl}_2$ (**3**·0.6CH₂Cl₂) and $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ (**4**)

	1	2	3	4
Empirical formula	C ₈ H ₉ Cl ₃ N ₃ Mo	C ₁₆ H ₁₃ N ₁₂ S ₂ Re	C _{21.6} H _{17.2} Cl _{1.2} N ₉ OSRe	C ₂₃ H ₁₈ N ₇ OSRe
FW	419.52	623.70	679.64	626.70
Space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>Pbca</i>	<i>Pccn</i>
Unit cell dimensions				
<i>a</i> (Å)	13.046(2)	13.6408(7)	16.7996(7)	28.358(1)
<i>b</i> (Å)	14.584(3)	9.4510(5)	12.0644(5)	11.9504(5)
<i>c</i> (Å)	14.986(3)	16.7694(9)	22.448(1)	12.8376(6)
β (°)	90.00	113.216(1)	90.00	90.00
<i>V</i> (Å ³)	2851.3(9)	1986.8(2)	4549.6(3)	4350.4(3)
<i>Z</i>	8	4	8	8
<i>D</i> _{calc} (g cm ⁻³)	1.955	2.085	1.984	1.914
μ (cm ⁻¹)	14.84	63.60	56.12	57.15
No. of reflections	3509	4783	5595	5356
<i>a</i> <i>R</i> ₁	0.0451	0.0269	0.0427	0.397
<i>b</i> <i>wR</i> ₂	0.0592	0.0577	0.0934	0.0646

$$^a R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|.$$

$$^b wR_2 = \left[\Sigma \left[w(F_o^2 - F_c^2)^2 \right] / \Sigma \left[w(F_o^2)^2 \right] \right]^{1/2}$$

Table 2Selected bond lengths (Å) and angles (°) for [MoCl₃(η¹-NNC₄H₃N₂H)(η²-HNNHC₄H₃N₂)] (**1**)

Mo(1)–N(5)	1.741(3)	Mo(1)–Cl(2)	2.435(1)
Mo(1)–N(1)	1.939(4)	Mo(1)–Cl(1)	2.464(1)
Mo(1)–N(4)	2.232(4)	N(1)–N(2)	1.353(5)
Mo(1)–Cl(3)	2.398(1)	N(5)–N(6)	1.301(4)
N(5)–Mo(1)–N(1)	91.3(2)	Cl(3)–Mo(1)–Cl(2)	85.86(4)
N(5)–Mo(1)–N(4)	164.0(2)	N(5)–Mo(1)–Cl(1)	92.5(1)
N(1)–Mo(1)–N(4)	72.7(2)	N(1)–Mo(1)–Cl(1)	89.0(1)
N(5)–Mo(1)–Cl(3)	97.8(1)	Cl(3)–Mo(1)–Cl(1)	167.48(4)
N(1)–Mo(1)–Cl(3)	97.8(1)	N(4)–Mo(1)–Cl(1)	86.1(1)
N(4)–Mo(1)–Cl(3)	85.9(1)	Cl(2)–Mo(1)–Cl(1)	84.68(4)
N(5)–Mo(1)–Cl(2)	104.6(1)	N(2)–N(1)–Mo(1)	123.6(3)
N(1)–Mo(1)–Cl(2)	163.1(1)	N(6)–N(5)–Mo(1)	174.4(3)
N(4)–Mo(1)–Cl(2)	91.2(1)		

Table 3

Selected bond lengths (Å) and angles (°) for $[\text{Re}(\eta^1\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{S})(\eta^1\text{-NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)]$ (**2**)

Re(1)–N(1)	1.772(3)	Re(1)–S(2)	2.474(1)
Re(1)–N(5)	1.933(3)	S(1)–C(9)	1.765(4)
Re(1)–N(7)	2.120(3)	S(2)–C(13)	1.740(4)
Re(1)–N(11)	2.160(3)	N(1)–N(2)	1.230(4)
Re(1)–S(1)	2.3891(1)	N(5)–N(6)	1.332(4)
N(1)–Re(1)–N(5)	92.4(1)	N(11)–Re(1)–S(1)	90.89(8)
N(1)–Re(1)–N(7)	165.4(1)	N(1)–Re(1)–S(2)	96.7(1)
N(5)–Re(1)–N(7)	73.2(1)	N(5)–Re(1)–S(2)	100.9(1)
N(1)–Re(1)–N(11)	100.8(1)	N(7)–Re(1)–S(2)	88.48(8)
N(5)–Re(1)–N(11)	162.4(1)	N(11)–Re(1)–S(2)	66.15(9)
N(7)–Re(1)–N(11)	93.8(1)	S(1)–Re(1)–S(2)	154.69(3)
N(1)–Re(1)–S(1)	98.1(1)	N(2)–N(1)–Re(1)	178.8(3)
N(5)–Re(1)–S(1)	99.0(1)	N(6)–N(5)–Re(1)	127.4(3)
N(7)–Re(1)–S(1)	82.32(9)		

Table 4

Selected bond lengths (Å) and angles (°) for $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{NNC}_4\text{H}_3\text{N}_2)(\eta^2\text{-HNNC}_4\text{H}_3\text{N}_2)] \cdot 0.6\text{CH}_2\text{Cl}_2(\mathbf{3} \cdot 0.6\text{CH}_2\text{Cl}_2)$

Re(1)–N(5)	1.768(6)	Re(1)–N(9)	2.165(6)
Re(1)–N(1)	1.941(6)	Re(1)–S(1)	2.387(2)
Re(1)–O(1)	2.015(5)	N(1)–N(2)	1.326(8)
Re(1)–N(3)	2.154(6)	N(5)–N(6)	1.236(8)
N(5)–Re(1)–N(1)	93.9(2)	N(3)–Re(1)–N(9)	96.3(2)
N(5)–Re(1)–O(1)	99.5(2)	N(5)–Re(1)–S(1)	95.6(2)
N(1)–Re(1)–O(1)	98.8(2)	N(1)–Re(1)–S(1)	91.0(2)
N(5)–Re(1)–N(3)	167.1(2)	O(1)–Re(1)–S(1)	161.3(2)
N(1)–Re(1)–N(3)	73.3(2)	N(3)–Re(1)–S(1)	86.2(2)
O(1)–Re(1)–N(3)	81.5(2)	N(9)–Re(1)–S(1)	82.0(2)
N(5)–Re(1)–N(9)	96.6(2)	N(2)–N(1)–Re(1)	126.1(5)
N(1)–Re(1)–N(9)	167.9(2)	N(6)–N(5)–Re(1)	172.1(5)
O(1)–Re(1)–N(9)	85.4(2)		

Table 5

Selected bond lengths (Å) and angles (°) for $[\text{Re}(\eta^3\text{-SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{O})(\eta^1\text{-NNC}_5\text{H}_4\text{N})(\eta^2\text{-HNNC}_5\text{H}_4\text{N})]$ (**4**)

Re(1)–N(4)	1.779(6)	Re(1)–N(7)	2.142(5)
Re(1)–N(1)	1.946(5)	Re(1)–S(1)	2.398(2)
Re(1)–O(1)	2.074(4)	N(1)–N(2)	1.326(7)
Re(1)–N(3)	2.133(5)	N(4)–N(5)	1.245(7)
N(4)–Re(1)–N(1)	89.7(2)	N(3)–Re(1)–N(7)	93.9(2)
N(4)–Re(1)–O(1)	98.5(2)	N(4)–Re(1)–S(1)	92.6(2)
N(1)–Re(1)–O(1)	94.4(2)	N(1)–Re(1)–S(1)	94.7(2)
N(4)–Re(1)–N(3)	161.8(2)	O(1)–Re(1)–S(1)	165.7(2)
N(1)–Re(1)–N(3)	72.2(2)	N(3)–Re(1)–S(1)	87.0(1)
O(1)–Re(1)–N(3)	85.3(2)	N(7)–Re(1)–S(1)	81.6(1)
N(4)–Re(1)–N(7)	104.1(2)	N(2)–N(1)–Re(1)	128.0(4)
N(1)–Re(1)–N(7)	165.9(2)	N(5)–N(4)–Re(1)	173.5(5)
O(1)–Re(1)–N(7)	86.9(1)		

Table 6
Comparison of selected bonding parameters for structures containing the {M(HNNHR)} moiety

Compound	{M(NNR)} unit			{M(HNNR)} unit			{M(HNNHR)} unit			Ref.
	M-N	N-N	M-N-N	M-N	N-N	M-N-N	M-N	N-N	M-N-N	
[MoCl ₃ (η ¹ -NNC ₅ H ₄ NH)(η ² -HNNHC ₅ H ₄ N)]	1.756(8)	1.266(11)	170.0(3)				1.960(8)	1.375(10)	121.9(3)	[11]
[MoCl ₃ (η ¹ -NNC ₄ H ₃ N ₂ H)(η ² -HNNHC ₄ H ₃ N ₂)]	1.741(3)	1.301(4)	174.4(3)				1.939(4)	1.353(5)	123.6(3)	This work
[(C ₅ H ₅)Re(CO) ₂ {HNN(CH ₃)C ₆ H ₄ Me}][BF ₄]							1.949(9)	1.32(1)	139.1(7)	[19]
[ReO{HNNC(S)Ph}{HNNHC(S)Ph}]				2.022(9)	1.350(12)	124.2(6)	2.054(7)	1.379(9)	122.3(12)	[20]
[Re{HNNC(S)Ph}{HNNHC(S)Ph} ₂][Cl]				2.009(18)	1.347(21)	127.0(13)	1.965(18)	1.397(21)	127.3(12)	[21]
							1.989(15)	1.376(20)	123.0(12)	
[ReCl ₃ (η ¹ -NNC ₅ H ₄ NH)(η ² -HNNC ₅ H ₄ N)]	1.743(8)	1.249(12)	168.1(8)	1.934(9)	1.308(10)	127.1(8)				[11]