# MULTIPLE BONDS BETWEEN MAIN GROUP ELEMENTS AND TRANSITION METALS—LXXXI.\* CONDENSATION REACTIONS OF HIGH-VALENT PENTAMETHYLCYCLOPENTADIENYL RHENIUM COMPLEXES WITH THIOPHENOL AND DERIVATIVES: SYNTHETIC AND STRUCTURAL ASPECTS

# JANOS TAKACS,<sup>†</sup> PAUL KIPROF and WOLFGANG A. HERRMANN<sup>‡</sup>

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-8046 Garching (Germany)

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Abstract—The half-sandwich rhenium(VII) complex  $(\eta^5-C_5Me_5)ReO_3$  (1; Me = CH<sub>3</sub>) undergoes reduction with thiophenol giving the rhenium(V) condensation product ( $\eta^{5}$ - $C_3Me_3Ne(O)(SC_6H_3)_2$  (2a) in high yield. However, toluene-3,4-dithiol reacts only slowly with 1, with traces of the fully substituted rhenium(V) species  $(\eta^5-C_5Me_5)Re(1,2-S_2C_6H_3-$ 4-CH<sub>3</sub>)<sub>2</sub> (**3a**) being formed. The related N,S-chelating ligand 2-aminothiophenol forms the amido derivative  $(\eta^5 - C_5 Me_5)Re[1,2-S(HN)C_6H_4]_2$  (3b) in good yield. Compounds 3a and **3b** are also accessible by two alternative routes: (i) from  $(\eta^5-C_5Me_5)Re(O)Cl_2$  (4) and the corresponding thiols in the course of two-step substitution/condensation reactions via the intermediates  $(\eta^{5}-C_{5}Me_{5})Re(O)(1,2-S_{2}C_{6}H_{3}-4-CH_{3})$  (2b) and  $(\eta^{5}-C_{5}Me_{5})Re(O)[1,2-S_{2}C_{6}H_{3}-4-CH_{3})$  $S(HN)C_6H_4$  (2c), respectively; (ii) from the tetrachloro complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)ReCl<sub>4</sub> (5) and two equivalents of the respective ligands. Employing a 1:1 stoichiometry, reaction of  $(\eta^5 - C_5 Me_4 Et) ReCl_4$  (5';  $Et = C_2 H_5$ ) with 2-aminothiophenol yields the amidothiophenolato(N,S) complex of formula  $(\eta^5 - C_5 Mc_4 Et)Re[1,2-S(HN)C_6H_4]Cl_2$  (6'). The solidstate structure of the bis(dithiolato)rhenium(V) complex 3a was determined by means of X-ray diffraction techniques. The core geometry around the rhenium is almost perfectly square pyramidal, with the five-membered ring ligand occupying the apical position (centroid  $\pi$ -coordination), while the four sulphur atoms define the basal plane. The relatively short distances between the interligand sulphur atoms (297-301 pm) are compatible with possible bonding interactions, e.g. partial disulphide character.

High oxidation state half-sandwich organometallic compounds have received considerable attention in recent years. Thiolato transition metal complexes in medium to high oxidation states are also the focus of interest, not least because of their special relationship to biochemically relevant systems.<sup>1,2</sup> Finally, some emphasis on rhenium stems from the

‡ Author to whom correspondence should be addressed.

properties of the <sup>186</sup>Re and <sup>188</sup>Re isotopes that are candidates for certain radiopharmaceuticals for therapeutic applications.<sup>3</sup>

It was recently determined in our laboratory that condensation reactions of methyltrioxorhenium(VII), CH<sub>3</sub>ReO<sub>3</sub>, with catechols and similar *aromatic* bifunctional ligands of type HX···Y (X = O, S, Y = N, NH<sub>2</sub>, OH) provide a convenient route to novel hexacoordinate *cis*-dioxo(methyl) rhenium derivatives of  $d^0$  configuration.<sup>4,5</sup> In order to find out as to whether replacement of the  $\sigma$ bonded methyl group in CH<sub>3</sub>ReO<sub>3</sub> by the much bulkier pentamethylcyclopentadienyl  $\pi$ -ligand in ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)ReO<sub>3</sub> would entail a different reactivity pattern, ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)ReO<sub>3</sub> (1), ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Re(O)Cl<sub>2</sub>

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<sup>&</sup>lt;sup>†</sup>Currently Alexander von Humboldt Fellow on leave from the Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprem, Hungary.

(4),  $(\eta^{5}-C_{5}Me_{5})ReCl_{4}$  (5) and  $(\eta^{5}-C_{5}Me_{4}Et)ReCl_{4}$  (5') were investigated in their reactions with monoand bifunctional thiophenols. The synthetic results as well as the crystal structure of the bis (dithiolato) complex  $(\eta^{5}-C_{5}Me_{5})Re(1,2-S_{2}C_{6}H_{3}-4-CH_{3})_{2}$  (3a) are reported in the present publication.

#### **RESULTS AND DISCUSSION**

# (1) Rhenium(V) complexes derived from aromatic thiols

The reaction of  $(\eta^5-C_5Me_5)ReO_3$  (1) with thiophenol is slow at room temperature as compared to the fast condensation reaction of this ligand with CH<sub>3</sub>ReO<sub>3</sub>.<sup>6</sup> Addition of mineral acids (that promote the protonation of the oxo ligand, presumed to be the first step in the condensation) or of 2,2-dimethoxypropane (as water scavenger) somewhat increase the rate but not sufficiently. However, temperatures around 110°C (boiling toluene) effect high-yield formation of the half-sandwich oxo complex of formula ( $\eta^5$ -C<sub>5</sub>Me\_5)Re(O)(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (**2a**) according to eq. (1). This compound is also formed from ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Re(O)Cl<sub>2</sub> and thiophenolate,<sup>7</sup> but the new route reported here is more straightforward.

The process involves both *condensation* and *reduction* reactions as the heptavalent rhenium is reduced to oxidation state + V, with the thiol serving as reductant. Diphenyl disulphide [eq. (1)] was isolated and identified. Formation of the hypothetical rhenium(VII) condensation products such as  $(\eta^{5}-C_{5}Me_{5})Re(O)(SC_{6}H_{5})_{4}$  (in analogy to the stable CH<sub>3</sub>Re(O)(SC<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>6</sup> formed from CH<sub>3</sub>ReO<sub>3</sub>) or  $(\eta^{5}-C_{5}Me_{5})Re(O)_{2}(SC_{6}H_{5})_{2}$  does not occur. Due to the bulk of the pentamethylcyclopentadienyl and thiophenolate ligands, these complexes would sterically be more crowded than **2a**. Further condensation of **2a** to  $(\eta^{5}-C_{5}Me_{5})Re(SC_{6}H_{5})_{4}$  was not observed even upon prolonged reflux with thiophenol.



#### (2) Rhenium(V) complexes of toluene-3,4-dithiol

By way of contrast, reaction between 1 and toluene-3,4-dithiol under similar conditions is very slow. The starting compound 1 is recovered almost quantitatively after 2 h in refluxing toluene. This is surprising since both aromatic mono- and 1,2dithiols react with CH<sub>3</sub>ReO<sub>3</sub> cleanly with condensation.<sup>6</sup> This different reactivity is also puzzling, considering that the expected products ( $\eta^{5}$ - $C_5Me_5)Re(O)(1,2-S_2C_6H_3-4-CH_3)$  (2b) or ( $\eta^5$ - $C_5Me_5)Re(1,2-S_2C_6H_3-4-CH_3)_2$  (3a) are thermodynamically stable (vide infra). The difference in acidity of the dithiol does not impose a barrier on the condensation reaction (vide infra), and aromatic 1,2-dithiols are known to be stronger reductants than thiophenol.<sup>8</sup> On the other hand, they do not form simple disulphides but rather eight-membered  $(C_2S_2S_2C_2)$  ring systems.

The above-mentioned monosubstituted rhenium (V) compound **2b** was synthesized from **4** and stoichiometric amounts of thiolate generated from thiol/triethylamine (Scheme 1). *Aliphatic* congeners of **2b,c** with O,O-, O,S-, S,S-, and O,N-chelating ligands have been reported from analogous reactions.<sup>9</sup> The substitution reaction shown in Scheme 1 is fast. If one employs an *excess* of dithiol, however, a subsequent slow condensation with high-yield formation of the reddish bis(dithiolato) derivative **3a** takes place.

#### (3) Rhenium(V) complexes of 2-aminothiophenol

Counting the oxo ligand as a two- or a fourelectron donor, the half-sandwich rhenium(V) derivatives 2a,b are formally 16e- or 18e-species, respectively. Although they did not form adducts with Lewis base amine ligands, it seemed interesting to study the reaction of 1 and 4 with the bifunctional ligand 2-aminophenol, since formation of a fivemembered chelate ring with a  $N \rightarrow Re$  dative bond or, more common in high oxidation state oxo complexes, 5,10 deprotonation of the amino group could not be excluded. If a toluene solution of 1 in the presence of an excess of 2-aminothiophenol is boiled under reflux, the colour quickly turns green. A dark green compound was isolated and characterized as the novel rhenium(V) complex **3b** of formula  $(\eta^{5}-C_{5}Me_{5})Re[1,2-S(HN)C_{6}H_{4}]_{2}$ (Scheme 2).

The same condensation product **3b** can be obtained in good yields at room temperature starting from **4** and *two equivalents* of 2-amino-thiophenol in the presence of a base such as tricthylamine to deprotonate the aminothiol (Scheme 2). Consecutive colour changes in this particular case



Scheme 1.

indicated that the formation of the fully substituted product **3b** proceeds in two steps: the first step is fast (HCl elimination), while the second step (condensation) is slow. The yellow intermediate **2c** of formula  $(\eta^{5}-C_{5}Me_{5})Re(O)[1,2-S(HN)C_{6}H_{4}]$  was isolated in high yields (Scheme 2).

Another convenient route to the bis(dithiolato-S,S) and bis(amidothiophenolato-S,N) compounds **3a** and **3b**, respectively, commences from the tetrachloro complex ( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)ReCl<sub>4</sub> (**5**): treatment with two equivalents of toluene-3,4-dithiol and 2aminothiophenol in the presence of a base according to Schemes 1 and 2, respectively, gives **3a** and **3b** in greater than 85% isolated yield.

A yellow complex, 6, is formed when 5 and 2aminothiophenol react in equimolar amounts. The formula  $(\eta^5-C_5Me_5)ReCl_2[1,2-S(HN)C_6H_4]$  is tentatively assigned on the basis of the spectroscopic data. Complex 6 was also obtained by treatment of compound 2c with chlorotrimethylsilane, a reagent widely used to replace an oxo ligand by two chloro ligands. However, the isolation of analytically pure **6** was rendered impossible due to its low solubility in organic solvents. In order to gain increased solubility,  $(\eta^{5}-C_{5}Me_{4}Et)ReCl_{4}$  (5') was used in a similar reaction, and the yellow dichloro complex of formula  $(\eta^{5}-C_{5}Me_{4}Et)ReCl_{2}[1,2-S(HN)C_{6}H_{4}]$  (6') was in fact isolated in high yields and analytically pure [eq. (2)].





Attempted synthesis of  $(\eta^5-C_5Me_5)Re(SC_6H_5)_4$ starting from 5 and an excess of thiophenolate lead to an intractable, moisture-sensitive oil which yielded 2a upon hydrolysis.

#### (4) Spectroscopic data

All new compounds are thermally stable, and the condensation products 2a, 3a and 3b are stable against water. The <sup>1</sup>H NMR spectra of compounds 2c and 3b show that the amido protons resonate at 8.89 and 9.23 ppm, respectively. The chemical shifts of the NH protons in compounds 6 and 6', are 12.67 and 12.68 ppm, respectively. As an explanation of this strong low-field shift, one is tempted to invoke an interaction (hydrogen bridge) between the NH proton and the chloride ligands.

# CRYSTAL AND MOLECULAR STRUCTURE OF THE BIS(DITHIOLATE) RHENIUM(V) COMPLEX (3a)

Due to the asymmetry in the ligand toluene-3,4dithiol, the synthesis of **3a** (Scheme 1) gives rise to formation of *cis*- and *trans*-isomers. Crystallographic investigations of **3a** have shown that the crystal chosen for this study contained both isomers (Fig. 1). As a result, disorder of one methyl group in the 4-position [(C(57) and C(57')] occurs. The disorder at only one side of the molecule may arise from packing effects. Both methyl groups [C(57) and C(57')] were nevertheless refined with anisotropic displacement parameters and a site occupation factor of 0.5.

The core geometry around the rhenium atom can



Fig. 1. SCHAKAL drawing of compound **3a**. Hydrogen atoms are omitted for clarity. The disordered methyl group C(57)' is shown by dotted lines.

be described as square pyramidal, with the centre of the aromatic  $\pi$ -ligand located in the apical position and the four sulphur atoms forming the basal plane (Fig. 1). The rhenium atom lies 92 pm above this plane. All rhenium-to-sulphur distances are almost equal [231.8(1)-234.6(1) pm; Table 1] and are in the normal range for single bonds found in rhenium(V) thiolato complexes such as [Re(O)  $(SR)_4$ <sup>-11</sup> and  $[Re{(SCH_2)_3CCH_3}_2]^{-.12}$  The angles S-Re-S' are all close to 80°, and the sulphur-sulphur distances are almost the same within the ligands and between the two ligands, respectively. These distances cover the range between 298.5(3) and 307.4(3) pm (Table 1) so they hardly deviate from the data of the previously published bis( $\mu$ -sulphido) dinuclear compound [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)  $Re(O)(\mu-S)]_2$ .<sup>13</sup> It is also remarkable that the sulphur contacts between two different ligands are significantly smaller [298.5(3) and 300.5(3) pm] as compared to the contacts of two sulphur atoms of the same ligand [305.4(3) and 307.4(3) pm]. For

comparison, the sum of the van der Waals' radii is 360 pm; the S—S distance in the (monoclinic) elemental sulphur is 204 pm.<sup>14</sup> The relatively short interligand sulphur distances, e.g. the partial disulphide character of the toluene-3,4-dithiolate ligand is in our opinion due to both a repulsion effect of the sterically demanding  $C_5Me_5$  ligand and an electronic effect originating from the oxidation state of the metal. Disulphide complexes M(RSSR) of transition metals are relatively rare as compared to the large number of thiolate compounds  $M(SR)_2$ .<sup>15</sup> Complexes with thiolate ligands showing partial disulphide character are usually found for the high metal oxidation states, examples being  $[\text{Re}\{(\text{SCH}_2)_3\text{CCH}_3\}_2]^ [d(S-S): 283 \text{ pm}^{12}],$  $MoO_{2}[(R)_{2}NC(R)_{2}C(R)_{2}S]_{2}$  [d(S—S): 273–282 pm<sup>16</sup>], and/or have a sterically crowded environment around the metal atom such as in  $(\eta^5 - C_5 H_5)_2$ Mo(SR)<sub>2</sub>.<sup>17</sup> It is obvious that these two factors play an important role in the reductive elimination of organic disulphides from transition metal thiolato



Fig. 2. Packing of compound 3a (SCHAKAL).

| <b>Re</b> — <b>S</b> (1) | 232.0(2) | S(1)ReS(2)      | 82.35(5)  |
|--------------------------|----------|-----------------|-----------|
| ReS(2)                   | 231.8(1) | S(1)—Re— $S(3)$ | 134.08(5) |
| Re—S(3)                  | 234.6(1) | S(1)—Re— $S(4)$ | 79.69(5)  |
| ReS(4)                   | 234.0(1) | S(2)—Re— $S(3)$ | 80.25(6)  |
| S(1)—C(42)               | 171.4(6) | S(2)—Re— $S(4)$ | 133.16(6) |
| S(2) - C(41)             | 174.7(6) | S(3)—Re— $S(4)$ | 82.02(5)  |
| S(3)—C(51)               | 177.4(6) | Cp-Re-S(1)      | 114.0     |
| S(4)—C(52)               | 175.7(6) | Cp-Re-S(2)      | 114.8     |
| $S(1) \cdots S(4)$       | 298.5(3) | Cp-Re-S(3)      | 111.9     |
| $S(2) \cdots S(3)$       | 300.5(3) | Cp-Re-S(4)      | 112.0     |
| $S(1) \cdots S(2)$       | 305.4(3) |                 |           |
| $S(3) \cdots S(4)$       | 307.4(3) |                 |           |
| Re—Cp                    | 198.1    |                 |           |
|                          |          |                 |           |

Table 1. Selected bond lengths (pm), non-bonding distances (pm) and bond angles (°) for compound  $3a^a$ 

<sup>*a*</sup>Cp denotes the centre of the aromatic  $\pi$ -ligand  $[\eta^{5}-C_{5}(CH_{3})_{5}]$ .

complexes according to eq. (3).



An interesting feature of the structure is the *folding* of the toluene-3,4-dithiolate ligands along the S-S axis by 22.6(2) and 36.5(1)° off planarity yielding the envelope form of the five-membered ring Re-S -C-C-S. The related rhenium(V) complex  $(\eta^{5}-C_{5}Me_{5})Re(1,2-O_{2}C_{6}Cl_{4})_{2}$  contains practically planar catecholate ligands.<sup>23</sup> This difference may be attributed to the stronger  $\pi$ -donor properties of the oxygen atoms (catecholates have been shown to be good  $\pi$ -donor ligands) as compared to sulphur atoms, although packing effects as well as the interligand sulphur-sulphur interaction may also effect the observed ligand folding. It seems likely that the difference in the folding angles of the two toluene-3,4-dithiolate ligands is the result of packing effects (Fig. 2).

#### CONCLUSIONS

Condensation reactions of the half-sandwich oxo rhenium(VII) complex ( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)ReO<sub>3</sub> (1) with thiophenols proceed in a different manner than the analogous reactions of CH<sub>3</sub>ReO<sub>3</sub>. Reduction of the heptavalent rhenium to oxidation state V prevales, in spite of the fact that the electron-rich pentamethylcyclopentadienyl ligand is expected to make the rhenium less susceptible towards reduction as compared with CH<sub>3</sub>ReO<sub>3</sub>.\* We believe that reduction is facilitated by the bulkiness of the pentamethylcyclopentadienyl ligand which prevents the accomodation of the same number of thiolate and oxo ligands at rhenium as in the case of  $CH_3Re(O)(SR)_4$ . This steric requirement could also induce the observed reductive elimination of disulphides [eq. (3)]. 1,2-Aminothiophenol leads to a similar deprotonation of the amine function as in the case of CH<sub>3</sub>ReO<sub>3</sub>; an amido group attached to rhenium thus forms. The crystal structure of the half-sandwich compound  $(\eta^5-C_5Me_5)Re(1,2 S_2C_6H_3$ -4-CH<sub>3</sub>)<sub>2</sub> (3a) shows interaction between sulphur atoms of different toluene-3,4-dithiolate ligands, indicating some disulphide contribution to the overall structure. The chelate effect of the S,Sligand is likely to prevent disulphide elimination in this particular case.

#### EXPERIMENTAL

All reactions were carried out in a dry nitrogen atmosphere employing conventional Schlenk techniques. The starting compounds 1, 5, 5' and 4 were synthesized as described in the literature.<sup>22</sup> The thiols and 2-aminothiophenol were used as received from Aldrich Chemicals. The <sup>1</sup>H NMR spectra were recorded at 25°C and 400 MHz (JEOL JNM GX-400), electron-impact mass spectra at 70 eV (Finnigan MAT 311-A). The mass spectra are based on the <sup>187</sup>Re and <sup>35</sup>Cl isotopes (m/z values).

### (1) Synthesis of $oxo(\eta^5$ -pentamethylcyclopentadienyl)bis(thiophenolato)rhenium(V) (2a)

To 1 (73.8 mg, 0.2 mmol) in 10 cm<sup>3</sup> of toluene, thiophenol  $(81 \times 10^{-3} \text{ cm}^3, 0.8 \text{ mmol})$  was added.

<sup>\*</sup> Studies on the electrochemistry of CH<sub>3</sub>ReO<sub>3</sub> and  $(\eta^5 - C_5Me_5)ReO_3$  support this view (W. A. Herrmann and R. Albach, unpublished results).

The solution was refluxed for 2–3 h, then cooled down to room temperature. After filtration and concentration of the solution to 2–3 cm<sup>3</sup> *in vacuo*, n-hexane was added to precipitate the product as a yellowish-brown solid. Recrystallization from toluene–n-hexane at –30°C yielded analytically pure **2a**. Yield 79 mg (71%). Found (Calc.): C, 47.1 (47.5); H, 4.9 (4.5); Re, 33.3 (33.5); S, 11.3 (11.5)%. IR (KBr; cm<sup>-1</sup>): 923 vs [v(Re=O)], 2962 m, 2915 m, 1577 s, 1465 s, 1381 s. <sup>1</sup>H NMR (CDCl<sub>3</sub>; ppm):  $\delta(C_5Me_5)$  1.64 (s, 15H),  $\delta(C_6H_5)$  7.15–7.72 (m, 10H). EI–MS (*m*/*z*; rel. int. %): 556 ([M]<sup>+</sup>), 447 ([M –SC<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 65%), 370 ([C<sub>5</sub>Me<sub>5</sub>ReOS]<sup>+</sup>, 100%).

# (2) Synthesis of $oxo(\eta^{5}-pentamethylcyclopenta$ dienyl)(toluene-3,4-dithiolato-S,S')rhenium(V) (2b)

To 4 (81.6 mg, 0.2 mmol) dissolved in 10 cm<sup>3</sup> of toluene and 4 cm<sup>3</sup> of n-hexane, toluene-3,4-dithiol  $(26 \times 10^{-3} \text{ cm}^3, 0.2 \text{ mmol})$ , and triethylamine  $(56 \times 10^{-3} \text{ cm}^3, 0.44 \text{ mmol})$  were added under vigorous stirring. The green solution turned yellow and triethylammonium chloride precipitated. After 3-4 min the solution was filtered through 2 cm of silvlated silica (Merck No. 7719, 70-230 mesh), then the volume was reduced to 2-3 cm, and finally nhexane was added. A yellowish-brown microcrystalline solid precipitated. The mother liquor was decanted and the product was washed twice with n-hexane and dried in vacuo. Recrystallization from toluene-n-hexane at  $-30^{\circ}$ C afforded analytically pure 2b. Yield 89 mg (90%). Found (Calc.): C, 41.8 (41.5); H, 4.1 (4.3)%.

IR (KBr; cm<sup>-1</sup>): 920 sh, 912 s [ $\nu$ (Re=O)], 2917 w, 1456 m, 1376 m, 1026 w, 808 s, 548 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>; ppm):  $\delta$ (C<sub>5</sub>Me<sub>5</sub>) 2.04 (s, 15H);  $\delta$ (1,2-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-4-CH<sub>3</sub>) 2.35 (s, 3H);  $\delta$ (5-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>) 6.77 (d, 1H, <sup>3</sup>J = 7.7 Hz);  $\delta$ (3-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>) 7.63 (s, 1H);  $\delta$ (6-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>) 7.70 (d, 1H, <sup>3</sup>J = 7.7 Hz). EI-MS (m/z; rel. int. %): 492 ([M]<sup>+</sup>, 100); 135 ([C<sub>10</sub>H<sub>15</sub>]<sup>+</sup>, 10).

# (3) Synthesis of $oxo(n^5$ -pentamethylcyclopentadienyl)(1,2-amidothiophenolato-S,N)rhenium(V) (2c)

A procedure similar to the synthesis of **2b** was used starting from **4** (81.6 mg, 0.2 mmol), 2-aminothiophenol  $(24 \times 10^{-3} \text{ cm}^3, 0.22 \text{ mmol})$  and triethylamine  $(61 \times 10^{-3} \text{ cm}^3, 0.44 \text{ mmol})$ . Yield 72 mg (78%). Found (Calc.): C, 41.8 (41.7); H, 4.7 (4.4); N, 3.0 (3.0)%.

IR (KBr; cm<sup>-1</sup>): 3321 m [ $\nu$ (N—H)], 906 s [ $\nu$ (Re=O)], 3055 w, 2920 w, 1467 m, 1444 m, 1376

m, 1297 m, 1022 w, 851 m, 754 s, 709 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>; ppm):  $\delta$ (C<sub>5</sub>Me<sub>5</sub>) 1.98 (s, 15H);  $\delta$ (HNC<sub>6</sub>H<sub>4</sub>S) 6.63–7.57 (m, 4H);  $\delta$ (HNC<sub>6</sub>H<sub>4</sub>S) 8.89 (br, 1H). EI–MS (*m*/*z*; rel. int. %): 461 ([M]<sup>+</sup>, 100).

# (4) Synthesis of $(\eta^{5}$ -pentamethylcyclopentadienyl) bis(toluene-3,4-dithiolato-S,S')rhenium (V) (3a)

Method (a), from 4. To 4 (81.6 mg, 0.2 mmol) dissolved in toluene (8 cm<sup>3</sup>), toluene-3,4-dithiol  $(58 \times 10^{-3} \text{ cm}^3, 0.44 \text{ mmol})$  and triethylamine  $(56 \times 10^{-3} \text{ cm}^3, 0.4 \text{ mmol})$  in 2 cm<sup>3</sup> methanol were added. The stirring was continued for 48 h at room temperature, then the dark brown-red precipitate was filtered, washed with small amounts of water and then cold methanol and finally dried *in vacuo*. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-n-hexane at  $-30^{\circ}$ C yielded 97 mg (89%) of **3a**.

Method (b), from 5. A similar procedure as above starting from 5 (93 mg, 0.2 mmol) in toluene (5 cm<sup>3</sup>), and toluene-3,4-dithiol  $(58 \times 10^{-3} \text{ cm}^3, 0.44 \text{ mmol})$  as well as triethylamine  $(122 \times 10^{-3} \text{ cm}^3, 0.88 \text{ mmol})$  in methanol (5 cm<sup>3</sup>) yielded **3a** in 86% yield. Found (Calc.): C, 45.9 (45.8); H, 4.3 (4.3); Re, 29.9 (29.6)%.

IR (KBr; cm<sup>-1</sup>): 2912 w, 1578 m, 1373 s, 1285 m, 1206 m, 1094 m, 1022 m, 813 sh, 798 s, 692 s, 545 m, 436 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>; ppm):  $\delta$ (C<sub>5</sub>Me<sub>5</sub>) 1.71 (s, 15H),  $\delta$ (1,2-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-4-CH<sub>3</sub>) 2.34 (s, 6H),  $\delta$ (5-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>) 6.79 (d, 2H, <sup>3</sup>J = 7.9 Hz),  $\delta$ (3-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>) 7.51 (S, 2H);  $\delta$ (6-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>) 7.57 (d, 2H, <sup>3</sup>J = 7.9 Hz). EI-MS (*m*/*z*; rel. int. %): 630 ([M]<sup>+</sup>, 100), 135 ([C<sub>10</sub>H<sub>15</sub>]<sup>+</sup>, 33).

## (5) Synthesis of $(\eta^{5}$ -pentamethylcyclopentadienyl) bis(1,2-amidothiophenolato-S,N)rhenium (**3b**)

Method (a), from 1. To 1 (73.8 mg, 0.2 mmol) dissolved in toluene (10 cm<sup>3</sup>), 2-aminothiophenol  $(86 \times 10^{-3} \text{ cm}^3, 0.8 \text{ mmol})$  was added and the mixture was refluxed for 1.5 h. After cooling to 25°C, the solution was filtered and concentrated to 3 cm<sup>3</sup> *in vacuo*. Upon addition of n-hexane (15 cm<sup>3</sup>), an olive-green precipitate formed which was filtered and dried *in vacuo*. The product was recrystallized from THF-n-hexane at  $-30^{\circ}$ C. The dark olivegreen crystals contain 0.5 mol of the solvent THF per mol of **3b**. Yielded 91 mg (75%).

Method (b), from 4. To 4 (81.6 mg, 0.2 mmol) dissolved in 10 cm<sup>3</sup> of toluene, 2-aminothiophenol  $(47 \times 10^{-3} \text{ cm}^3, 0.44 \text{ mmol})$  and triethylamine  $(70 \times 10^{-3} \text{ cm}^3, 0.5 \text{ mmol})$  were added under stirring. The colour turned yellow, while triethyl-

| (a) | Crystal parameters<br>Empirical formula<br>Formula weight<br>Crystal colour and shape<br>Crystal dimensions (mm)<br>Radiation<br>Temperature (°C)<br>Space group<br>a (pm)<br>b (pm)<br>c (pm)<br>$\alpha$ (°)<br>$\beta$ (°)<br>$\gamma$ (°)<br>V (pm <sup>3</sup> )<br>Z<br>$\rho$ (calc.) (g cm <sup>-3</sup> )<br>$\mu$ (Mo- $K_{\alpha}$ ) (cm <sup>-1</sup> ) | C <sub>24</sub> H <sub>27</sub> S <sub>4</sub> Re<br>631.9<br>Red, thin plates<br>$0.72 \cdot 0.34 \cdot 0.03$<br>Mo- $K_{\alpha}$ ( $\lambda = 71.073 \text{ pm}$ )<br>$22 \pm 2$<br>$P\bar{1}$ (Int. Tab. No. 2)<br>744.5(4)<br>839.7(5)<br>2090(2)<br>85.03(4)<br>89.49(4)<br>64.72(6)<br>1177 × 10 <sup>6</sup><br>2<br>1.784<br>55.9  |
|-----|---|--|
| (b) | Data collectionDiffractometerMonochromatorScan typeScan time (s)Scan width (°)Maximum $2\theta$ (°)Number of reflections measuredNumber of independent reflectionsCorrectionsStandard reflections   | CAD4 Enraf-Nonius<br>Graphite, incident beam<br>$\omega$ -Scan<br>Maximum 60<br>$(1.40 + 0.30 \cdot tg\theta) \pm 25\%$ for corrections<br>50<br>8227 (-8/8; -10/10, -24/24)<br>3951<br>Lorentz-polarization,<br>$(F_c(\text{corr}) = F_c/(1 + \varepsilon \cdot F_c^2 \cdot LP)]$<br>numerical absorption corr.<br>(6 Faces, transmission range : 0.219-0.835)<br>3 every 3600 s intensity check<br>3 every 200 orientation check |
| (c) | Refinement<br>Solution<br>Hydrogen atoms<br>Refinement<br>Minimization function<br>Weighting scheme<br>Anomalous dispersion<br>Number of reflections included, NO<br>Number of parameters refined, NV<br>R<br>$R_w$<br>Goodness-of-fit<br>Residual $\Delta \rho$ (e <sup>-</sup> /Å <sup>3</sup> )<br>Shift/error   | Patterson method<br>All calculated, not refined<br>Full-matrix least-squares<br>$\Sigma w( F_o  -  F_c )^2$<br>$1/\sigma(F_o)^2$<br>All non-hydrogen atoms<br>3950 $I \ge 0.0$<br>271<br>$0.049^a$<br>$0.039^b$<br>2.886 <sup>c</sup><br>+1.43 near Re<br>-1.84<br>0.00  |

Table 2. Crystallographic data, parameters of data collection and structure refinement for 3a

<sup>a</sup>  $R = \Sigma(||F_o| - |F_c|)/\Sigma |F_o|.$ <sup>b</sup>  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$ <sup>c</sup> GOF =  $[\Sigma w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}.$ 

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ammonium chloride precipitated. After ca 5–10 min, the colour slowly started to turn green. The stirring was continued for 3 days. The volatiles were then removed *in vacuo*. The residue was extracted with toluene, the green solution was filtered and concentrated to ca 2–3 cm<sup>3</sup>. Upon addition of n-hexane, a green precipitate of **3b** formed which was recrystallized from THF–n-hexane at  $-30^{\circ}$ C. Yield 96 mg (87%).

*Method* (c), *from* 5. A procedure similar to (b) starting from 5 (93 mg, 0.2 mmol), 2-aminothiophenol  $(47 \times 10^{-3} \text{ cm}^3, 0.44 \text{ mmol})$  and triethylamine  $(140 \times 10^{-3} \text{ cm}^3, 1.0 \text{ mmol})$  yielded **3b** in 87% yielded. Found (Calc. for **3b**  $\cdot$  0.5 THF): C, 47.6 (47.7); H, 4.7 (4.8); N, 4.7 (4.6); Re, 30.6 (30.8)%.

IR (KBr; cm<sup>-1</sup>): 3294 m [ $\nu$ (N—H)], 3053 w, 2908 w, 1569 m, 1442 m, 1375 m, 1301 s, 1023 m, 746 s, 726 m, 704 m, 459 m, 436 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>; ppm):  $\delta$ (C<sub>5</sub>Me<sub>5</sub>) 1.66 (s, 15H),  $\delta$ (HNC<sub>6</sub>H<sub>4</sub>S) 6.64–7.47 (m, 8H);  $\delta$ (HNC<sub>6</sub>H<sub>4</sub>S) 9.23 (br, 2H). EI–MS (m/z; rel. int. %): 568 ([M]<sup>+</sup>, 90): 135 ([C<sub>5</sub>Me<sub>5</sub>]<sup>+</sup>, 10); 124 ([SC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>]<sup>+</sup>, 100).

 (6) Synthesis of dichloro(η<sup>5</sup>-tetramethylethylcyclopentadienyl)(1,2 - amidothiophenolato - S,N)rhenium
(V) (6')

To 5' (119.2 mg, 0.25 mmol) dissolved in 20 cm<sup>3</sup> of THF, 2-aminothiophenol  $(27.0 \times 10^{-3} \text{ cm}^3, 0.25)$ mmol) and anhydrous sodium carbonate (1-2 g powder) were added under vigorous stirring. The colour immediately turned to intense yellow. After 5 min, the solution was filtered, and the  $Na_2CO_3$ was washed with THF. The combined THF fractions were evaporated to dryness. The residue was taken up in methylenechloride and was filtered through silvlated silica (ca 3 cm). The filtrate was then concentrated in vacuo. Upon addition of n-hexane, a bright yellow microcrystalline solid separated, which was filtered and washed with n-hexane. Recrystallization from methylenechloriden-hexane yielded 104 mg (79%) of analytically pure 6'. Found (Calc.): C, 38.0 (38.5); H, 4.2 (4.2); N, 2.6 (2.6); Re, 35.0 (35.2)%.

IR (KBr; cm<sup>-1</sup>): 3224 s [ $\nu$ (N—H)], 2965 m, 2927 m, 1477 m, 1454 m, 1376 m, 1263 w, 1031 m, 1019 m, 821 w, 761 s. <sup>1</sup>H NMR (CDCl<sub>3</sub>; ppm):  $\delta$ (C<sub>5</sub>Me<sub>4</sub> CH<sub>2</sub>CH<sub>3</sub>) 0.96 (t, 3H, <sup>3</sup>J = 7.4 Hz);  $\delta$ (C<sub>5</sub>Me<sub>4</sub> CH<sub>2</sub>CH<sub>3</sub>) 1.62 (q, 2H, <sup>3</sup>J = 7.4 Hz);  $\delta$ (C<sub>5</sub>[CH<sub>3</sub>]<sub>4</sub> CH<sub>2</sub>CH<sub>3</sub>) 1.71, 1.74, 1.77, 1.81 (4S, 12H);  $\delta$ (1,2-S(NH)C<sub>6</sub>H<sub>4</sub>) 7.14–7.93 (m, 4H);  $\delta$ (1,2-S (NH)C<sub>6</sub>H<sub>4</sub>) 12.68 (br, 1H). EI–MS (*m*/*z*; rel. int. %): 529 ([M]<sup>+</sup>, 2); 493 ([M –HCl]<sup>+</sup>, 3); 125 ([H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>S]<sup>+</sup>, 100). (7) X-ray diffraction study of  $(\eta^{5}-pentamethyl-cyclopentadienyl)bis(toluene - 3,4 - dithiolato - S,S') rhenium(V) <math>(3a)^{18-21}$ 

Details of the data collection and structure refinement are listed in Table 2. The data were collected on a CAD4 (Enraf-Nonius). All computations were carried out on VAX 8200 and VAX 11/730 computers with the computer programs SDP<sup>18</sup> and SCHAKAL,<sup>19</sup> in the STRUX-II<sup>21</sup> system. Scattering factors were taken from ref. 20.

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