

Reactivity of Rhenium(I) Pseudo-allyl Complexes with Heterocumulenes. Part 2.† Insertion Reactions. Crystal structures of the Thiazolyl-thioureido and -dithiocarbamate Complexes $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{NPh})\text{NMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ and $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ ($\text{C}_3\text{H}_2\text{NS} = \text{thiazol-2-yl}$)

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The compound $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{mat})]$ [$\text{mat} = \text{anion of 2-(methylamino)thiazole}$] reacts under anhydrous conditions with an excess of PhNCS or CS_2 to give the thioureido rhenium(I) derivative $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{NPh})\text{NMe}(\text{C}_3\text{H}_2\text{NS})\}]$ (**1**) and the dithiocarbamate rhenium(I) complex $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]$ (**2**) respectively ($\text{C}_3\text{H}_2\text{NS} = \text{thiazol-2-yl}$). They are obtained by formal insertion of the heterocumulene into the Re-N bond. Compound (**1**) is triclinic, space group $P\bar{1}$, with $a = 15.058(6)$, $b = 14.305(6)$, $c = 12.371(6)$ Å, $\alpha = 108.51(3)$, $\beta = 75.16(3)$, $\gamma = 104.91(3)^\circ$ and $Z = 2$. The structure was refined to the final conventional R of 0.055. The rhenium atom is six-coordinate distorted octahedral. The organic ligand chelates through the nitrogen atom of the thiazole ring and the sulphur atom of the PhNCS moiety, and together with the metal forms a non-planar six-membered ring. Selected bond distances are: Re-P 2.436 (mean), Re-C 1.89 (mean), Re-N 2.20(1), Re-S 2.471(3) Å. Compound (**2**) is monoclinic, space group $P2_1/n$, with $a = 21.305(5)$, $b = 17.873(5)$, $c = 11.455(7)$ Å, $\beta = 97.81(3)^\circ$, and $Z = 4$. The structure was refined to the conventional R of 0.052. The rhenium atom is six-coordinate distorted octahedral. The organic ligand chelates through the two sulphur atoms of the CS_2 moiety and together with the metal forms a planar four-membered ring. Selected bond distances are: Re-P 2.431 (mean), Re-S 2.513 (mean), and Re-C 1.88 Å (mean).

The chemistry of heterocumulenes such as CS_2 , PhNCO , PhNCS , and COS with transition-metal complexes is still of current interest because these small molecules are structurally related to carbon dioxide and thus their metal complexes may be regarded as model compounds for CO_2 activation. Besides the normal modes of co-ordination (σ or η^2), these ligands can undergo dimerization,¹ disproportionation,² or insertion into a M-X bond ($\text{X} = \text{H, N, or C}$).³

We have previously reported⁴ on reactions of the aminothiazolato rhenium(I) complex $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{mat})]$ [$\text{mat} = \text{anion of 2-(methylamino)thiazole}$] and the formamido rhenium(I) complex $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{O}=\text{C}=\text{CH}=\text{NC}_6\text{H}_4\text{Me-}p)]$ with the heterocumulenes RNCs ($\text{R} = \text{Ph or } p\text{-MeC}_6\text{H}_4$). Reactions under non-anhydrous conditions occur with displacement of the starting chelate ligands and formation of the monothio- and dithio-carbamate complexes $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{O}-\text{C}(\text{NHR})=\text{S}\}]$ and $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}=\text{C}(\text{NHR})-\text{S}\}]$, respectively.⁴ The monothiocarbamate complexes are probably obtained *via* the intermediate formation of the corresponding monothiocarbamic acids. Thus seems to exclude a reaction in which the heterocumulene ligands give rise to a formal insertion into the Re-N bond.

In order to verify this assumption we have now investigated the reactions of PhNCS and CS_2 with $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{mat})]$

under anhydrous conditions. Thus thioureido and dithiocarbamate rhenium(I) derivatives have been obtained by formal insertion of PhNCS and CS_2 into the Re-N bond.

The crystal structures of the thiazolylthioureido complex $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{NPh})\text{NMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (**1**) and of the dithiocarbamate derivative $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (**2**) ($\text{C}_3\text{H}_2\text{NS} = \text{thiazol-2-yl}$) have been determined by X-ray crystallography.

Results and Discussion

A benzene solution of $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{mat})]$ reacts with an excess of PhNCS at reflux to give pale yellow crystals of the thiazolylthioureido complex $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{NPh})\text{NMe}(\text{C}_3\text{H}_2\text{NS})\}]$ (**1**), arising from formal insertion of PhNCS into the Re-N (amino) bond of the starting chelate ligand. This insertion gives rise to an expansion of the four-membered chelate ring to a six-membered one. The central metal atom is co-ordinated by the thiazole nitrogen and the sulphur atom of the PhNCS .

When the reaction is carried out with an excess of CS_2 , yellow crystals of the dithiocarbamate derivative $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]$ (**2**) are obtained in poor yield. In this complex the formal insertion of CS_2 into the Re-N (amino) bond gives rise to a four-membered ring through the two sulphur atoms of the CS_2 molecule linked to the metal.

The i.r. spectra show the presence of the phosphine and of two *cis* terminal carbonyl groups at the expected frequencies.⁵ The bands at 1550 and 1520 cm^{-1} in (**1**) are indicative of the presence of $\text{C}=\text{N}$ groups,⁶ whereas no bands are observed in this range for (**2**). The CH proton doublets in the ^1H n.m.r. spectra show a decrease in aromaticity of the thiazole ring in the

† Part 1 is ref. 4.

‡ Dicarboxyl{[methyl(thiazol-2-yl)amino](phenylimino)methanethiolato- SN^3 }bis(triphenylphosphine)rhenium(I)-dichloromethane (1/1) and dicarboxyl{[methyl(thiazol-2-yl)]dithiocarbamate- SS^2 }bis(triphenylphosphine)rhenium(I)-dichloromethane (1/1) respectively.

Supplementary data available: see Instruction for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

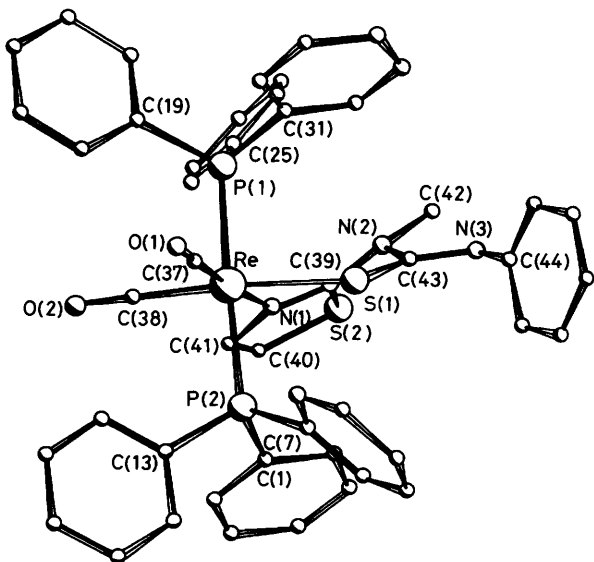


Figure 1. The crystal structure of $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{NPh})\text{NMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (1)

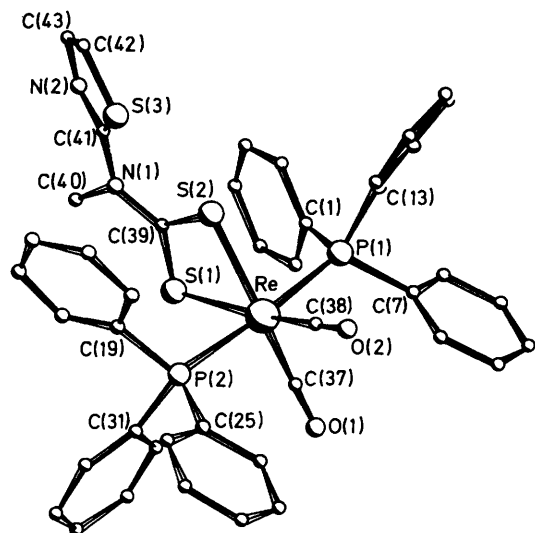


Figure 2. The crystal structure of $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (2)

order: complex (2) > free ligand > complex (1) > starting complex; this trend is also observed for the methyl protons.

Unlike the monothiocarbamate derivatives described in Part 1 of this series,⁴ the complexes here are not formed when the reaction is carried out at room temperature, only the starting compound is recovered. That the formation of the monothiocarbamate derivatives proceeds *via* an insertion reaction would therefore seem to be excluded. Instead the experimental data support the intermediate formation of the monothiocarbamic acid and subsequent electrophilic attack of its acid proton on the lone pair of a nitrogen atom co-ordinated to the metal.

X-Ray Structures of $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{NPh})\text{NMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (1) and $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (2).—The crystal structures of (1) and (2)

Table 1. Selected bond distances (Å) and angles (°) for (1). The CH_2Cl_2 molecule is disordered (see text)

| | | | |
|----------------|----------|---------------|----------|
| Re-P(1) | 2.426(4) | Re-N(1) | 2.20(1) |
| Re-P(2) | 2.446(4) | Re-C(37) | 1.89(2) |
| Re-S(1) | 2.471(3) | Re-C(38) | 1.89(1) |
| C(37)-Re-C(38) | 89.9(6) | P(2)-Re-S(1) | 82.7(2) |
| N(1)-Re-C(38) | 92.2(6) | P(1)-Re-C(37) | 88.0(5) |
| N(1)-Re-C(37) | 176.9(5) | P(1)-Re-C(38) | 90.2(4) |
| S(1)-Re-C(38) | 173.9(5) | P(1)-Re-N(1) | 89.7(3) |
| S(1)-Re-C(37) | 94.3(5) | P(1)-Re-S(1) | 94.3(2) |
| S(1)-Re-N(1) | 83.8(3) | Re-S(1)-C(43) | 113.1(5) |
| P(2)-Re-C(38) | 92.8(4) | Re-C(37)-O(1) | 177.0(1) |
| P(2)-Re-C(37) | 92.3(5) | Re-C(38)-O(2) | 177.0(1) |
| P(2)-Re-N(1) | 89.9(4) | P(1)-Re-P(2) | 177.0(2) |

Table 2. Selected bond distances (Å) and angles (°) for (2)

| | | | |
|----------------|----------|-----------------|----------|
| Re-P(1) | 2.430(2) | Re-S(2) | 2.512(3) |
| Re-P(2) | 2.432(3) | Re-C(37) | 1.87(1) |
| Re-S(1) | 2.514(3) | Re-C(38) | 1.89(1) |
| C(37)-Re-C(38) | 93.7(5) | P(2)-Re-C(37) | 91.5(3) |
| S(1)-Re-C(37) | 98.8(4) | P(2)-Re-C(38) | 90.7(3) |
| S(1)-Re-C(38) | 165.7(4) | P(1)-Re-P(2) | 175.5(1) |
| S(2)-Re-C(37) | 166.0(4) | Re-C(37)-O(1) | 177.0(1) |
| S(2)-Re-C(38) | 99.2(4) | Re-C(38)-O(2) | 179.0(1) |
| S(1)-Re-S(2) | 69.1(1) | Re-S(1)-C(39) | 88.3(4) |
| P(1)-Re-C(37) | 89.1(3) | Re-S(2)-C(39) | 88.2(4) |
| P(1)-Re-C(38) | 93.7(3) | S(1)-C(39)-S(2) | 114.4(6) |
| P(1)-Re-S(1) | 93.3(1) | S(1)-C(39)-N(1) | 121.0(8) |
| P(1)-Re-S(2) | 84.8(1) | S(2)-C(39)-N(1) | 124.6(8) |

are shown in Figures 1 and 2 respectively. Selected bond distances and angles are listed in Tables 1 and 2 for (1) and (2) respectively. The rhenium atoms are six-co-ordinate distorted octahedral in each case, with major asymmetries in the bond angles due to the geometrical constraints of the chelate ligands, and in the bond distances due to the variety and dimensions of the donor atoms. The Re-P [mean 2.43 Å in (1) and (2)] and Re-C [mean 1.89 Å in (1) and 1.88 Å in (2)] distances compare well with several other *trans* Re^I-P and *cis* Re^I-C determinations,^{4,5,7-9} and also the CO bond distances (mean 1.165 Å) are normal for these type of compounds.

In complex (1) the Re-N distance of 2.20(1) Å can be compared with 2.22(1) and 2.25(1) Å found in $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{mat})]$,⁵ whereas the Re-S bond distance of 2.471(3) Å can be compared with 2.51 Å (mean) found in $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{S}_2\text{CH})]$ ¹⁰ or with values varying from 2.38 to 2.47 Å in two Re^V dithiocarbamates.¹¹ The equatorial SNC₂ atoms are approximately coplanar. Mean planes calculations show that the SN₂C₂ ligand atoms of the six-membered-chelate ring are roughly coplanar while Re is completely out of this plane (by 0.93 Å) since the ligand makes a dihedral angle of *ca.* 30° with the equatorial plane. The planar thiazole ring is in turn inclined by *ca.* 20° with respect to the SN₂C₂ moiety and by *ca.* 30° to the equatorial plane, whereas the phenyl group is approximately perpendicular to these planes.

Double bonds in the thiazole are well localized in C(40)=C(41) [1.36(2) Å] and N(1)=C(39) [1.31(2) Å] whereas the C-S(2) distances (mean 1.73 Å) are typical for C(*sp*²)-S single bonds.¹² Structural details in the rest of the ligand are normal and need no particular comment. The N(3)-C(43) bond is essentially double with 1.30(2) Å, while the C(43)-S(1) bond, with a distance of 1.70(1) Å, also seems to participate to some

extent in a mesomeric distribution of the π -electron density with the contiguous N(3)–C(43) bond [1.30(2) Å].

In complex (2) the Re–S distances (mean 2.513 Å) agree well with the mean value of 2.51 Å found in [Re(CO)₂-(PPh₃)₂(S₂CH)]¹⁰ and 2.52 Å in co-crystallized monothio- and dithio-carbamate derivatives.⁴ The equatorial S₂C₂ atoms are slightly staggered with respect to the mean plane, whereas Re lies in the plane. The S₂CN moiety is perfectly planar and is inclined by only 2° to the equatorial plane, while the heterocycle forms dihedral angles of 27 and 29° with the above planes. Double bonds in the five-membered heterocycle are relatively well localized in C(41)=N(2) [1.35(2) Å] and C(42)=C(43) [1.34(5) Å]; however the S(3)–C distances of 1.70(2) and 1.71(3) Å are slightly shorter than expected for a C(sp²)–S single bond,¹² suggesting that the S atom should be in some way involved in delocalization of the π -electron density over the ring. On the other hand the C–S–C angle of 90.6° indicates that this atom is not hybridized.

That the two Re–S distances, as well as the two C(39)–S distances [S(1)–C(39) 1.69(1), S(2)–C(39) 1.70(1) Å], are chemically equivalent shows that both sulphur atoms have homogeneous behaviour toward Re and that, upon co-ordination, the π -electron density of the ligand is statistically distributed over the metallacycle. Partial double-bond character must be attributed also to the N(1)–C(39) [1.35(1) Å] and N(1)–C(41) bonds [1.38(1) Å]; thus the mesomeric effect seems to extend to N(1), and to a small extent to C(41), favoured by the coplanarity of the system.

Experimental

Solvents were purified and dried before use. The starting complex [Re(CO)₂(PPh₃)₂(mat)] was prepared following the

literature method.⁵ PhNCS and CS₂ were commercially available. Other materials were reagent grade. All the syntheses were performed under argon. I.r. and ¹H n.m.r. spectra were recorded on Perkin-Elmer 577 and on Bruker WP 80-MHz spectrometers, respectively. Elemental analyses were performed on a Carlo Erba elemental analyzer, model 1106.

Synthesis of the Complexes.—[Re(CO)₂(PPh₃)₂{SC(NPh)-NMe(C₃H₂NS)}]·CH₂Cl₂ (1). A large excess of PhNCS was added to a dry benzene solution (25 cm³) of the starting complex [Re(CO)₂(PPh₃)₂(mat)] (0.166 mmol). After refluxing for 2 h n-heptane was added to the reaction mixture. The solid was filtered off and washed with EtOH and Et₂O. The product was purified by chromatography using a silica-gel plate (2 mm) [ethyl acetate–CH₂Cl₂ (5:95) as eluant]. The complex was crystallized from CH₂Cl₂–EtOH (7:3 v/v) (80%), m.p. 208 °C, white (Found: C, 57.9; H, 3.9; N, 4.1; S, 6.1. C₄₉H₄₀N₃O₂P₂ReS₂ requires C, 58.0; H, 4.0; N, 4.1; S, 6.3%). I.r. (Nujol): ν (CO) 1 910s, 1 830s; ν (CN) 1 550m, 1 520m; ν (chelate ligand) 1 210m cm⁻¹. ¹H N.m.r. (CDCl₃): δ , 6.52, 6.05 (2 H, d, CH), 2.72 (3 H, s, CH₃).

[Re(CO)₂(PPh₃)₂{S₂CNMe(C₃H₂NS)}]·CH₂Cl₂ (2). A large excess of CS₂ (0.37 cm³) was added to a dry benzene solution (25 cm³) of the starting complex (0.166 mmol). During refluxing the solution changed from yellow to red. After 1 h n-heptane was added to the reaction mixture. The solid was filtered off and washed with EtOH and pentane. The product was purified by chromatography using a silica-gel plate (2 mm) [ethyl acetate–CH₂Cl₂ (1:99) as eluant]. The complex was crystallized from CH₂Cl₂–EtOH (7:3 v/v) (15%), m.p. 200 °C, yellow (Found: C, 52.2; H, 3.7; N, 2.7; S, 9.6. C₄₃H₃₅N₂O₂P₂ReS₃ requires C, 54.0; H, 3.7; N, 2.9; S, 10.1%). I.r. (Nujol): ν (CO) 1 920s, 1 845s; ν (chelate ligand) 1 340 m, 1 280m cm⁻¹. ¹H N.m.r. (CDCl₃): δ ,

Table 3. Atomic co-ordinates for [Re(CO)₂(PPh₃)₂{SC(NPh)NMe(C₃H₂NS)}]·CH₂Cl₂ (1)

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|-------|-------------|-------------|-------------|-------|-------------|-------------|-------------|
| Re(1) | 0.706 52(4) | 0.739 12(4) | 0.565 34(5) | C(10) | 0.989 6(7) | 1.033 4(7) | 0.315 3(9) |
| P(1) | 0.666 3(2) | 0.719 4(2) | 0.760 8(3) | C(11) | 0.903 5(7) | 1.030 3(7) | 0.290 2(9) |
| P(2) | 0.748 8(2) | 0.768 4(2) | 0.372 7(3) | C(12) | 0.828 1(7) | 0.953 2(7) | 0.309 3(9) |
| S(1) | 0.751 2(2) | 0.924 1(2) | 0.629 1(3) | C(13) | 0.800 0(7) | 0.675 1(7) | 0.248 4(6) |
| S(2) | 0.410 8(2) | 0.832 1(3) | 0.656 1(4) | C(14) | 0.820 6(7) | 0.590 0(7) | 0.261 3(6) |
| N(1) | 0.566 2(7) | 0.769 9(7) | 0.586 3(9) | C(15) | 0.861 2(7) | 0.521 9(7) | 0.164 7(6) |
| N(2) | 0.567 9(7) | 0.924 0(7) | 0.742 0(9) | C(16) | 0.881 3(7) | 0.538 8(7) | 0.055 2(6) |
| N(3) | 0.667 6(7) | 1.075 8(8) | 0.761 5(10) | C(17) | 0.860 7(7) | 0.623 8(7) | 0.042 3(6) |
| O(1) | 0.902 7(7) | 0.707 6(8) | 0.551 7(10) | C(18) | 0.820 0(7) | 0.692 0(7) | 0.138 9(6) |
| O(2) | 0.637 1(8) | 0.514 0(7) | 0.467 9(10) | C(19) | 0.687 1(7) | 0.604 6(7) | 0.781 6(6) |
| C(37) | 0.827 4(10) | 0.717 5(9) | 0.556 1(12) | C(20) | 0.738 0(7) | 0.539 1(7) | 0.693 6(6) |
| C(38) | 0.665 5(9) | 0.599 4(9) | 0.504 7(12) | C(21) | 0.753 4(7) | 0.454 6(7) | 0.713 8(6) |
| C(39) | 0.527 0(9) | 0.843 4(10) | 0.661 3(11) | C(22) | 0.717 9(7) | 0.435 5(7) | 0.822 1(6) |
| C(40) | 0.413 5(10) | 0.721 1(12) | 0.546 9(16) | C(23) | 0.667 0(7) | 0.500 9(7) | 0.910 2(6) |
| C(41) | 0.501 5(10) | 0.699 2(11) | 0.519 8(13) | C(24) | 0.651 6(7) | 0.585 5(7) | 0.889 9(6) |
| C(42) | 0.502 0(10) | 0.976 9(10) | 0.837 0(12) | C(25) | 0.541 4(6) | 0.707 3(6) | 0.830 3(6) |
| C(43) | 0.660 7(9) | 0.980 1(9) | 0.713 1(10) | C(26) | 0.479 8(6) | 0.638 1(6) | 0.762 3(6) |
| C(45) | 0.787 1(8) | 1.166 6(9) | 0.639 2(8) | C(27) | 0.383 8(6) | 0.623 1(6) | 0.806 4(6) |
| C(46) | 0.869 5(8) | 1.237 2(9) | 0.624 5(8) | C(28) | 0.349 3(6) | 0.677 1(6) | 0.918 4(6) |
| C(47) | 0.919 3(8) | 1.281 9(9) | 0.714 7(8) | C(29) | 0.411 0(6) | 0.746 2(6) | 0.986 4(6) |
| C(48) | 0.886 9(8) | 1.256 0(9) | 0.819 5(8) | C(30) | 0.507 0(6) | 0.761 3(6) | 0.942 4(6) |
| C(49) | 0.804 5(8) | 1.185 4(9) | 0.834 2(8) | C(31) | 0.732 6(6) | 0.818 2(7) | 0.863 7(9) |
| C(44) | 0.754 7(8) | 1.140 7(9) | 0.744 1(8) | C(32) | 0.706 7(6) | 0.911 4(7) | 0.919 0(9) |
| C(1) | 0.648 2(7) | 0.781 6(6) | 0.325 4(8) | C(33) | 0.762 3(6) | 0.985 9(7) | 0.990 7(9) |
| C(2) | 0.604 3(7) | 0.702 1(6) | 0.245 2(8) | C(34) | 0.843 7(6) | 0.967 4(7) | 1.007 2(9) |
| C(3) | 0.521 1(7) | 0.708 1(6) | 0.220 1(8) | C(35) | 0.869 6(6) | 0.874 2(7) | 0.952 0(9) |
| C(4) | 0.481 8(7) | 0.793 6(6) | 0.275 1(8) | C(36) | 0.814 0(6) | 0.799 7(7) | 0.880 2(9) |
| C(5) | 0.525 7(7) | 0.873 1(6) | 0.355 3(8) | Cl(1) | 1.022 3(8) | 0.426 2(9) | 0.285 1(10) |
| C(6) | 0.609 0(7) | 0.867 1(6) | 0.380 4(8) | Cl(2) | 0.944 8(15) | 0.277 1(15) | 0.178 0(18) |
| C(7) | 0.838 8(7) | 0.879 1(7) | 0.353 4(9) | Cl(3) | 0.844 9(9) | 0.381 4(10) | 0.396 6(12) |
| C(8) | 0.924 8(7) | 0.882 2(7) | 0.378 5(9) | Cl(4) | 0.898 0(13) | 0.258 8(13) | 0.173 8(14) |
| C(9) | 1.000 3(7) | 0.959 3(7) | 0.359 4(9) | C(50) | 0.939 1(20) | 0.313 7(22) | 0.292 8(26) |

Table 4. Atomic co-ordinates for $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2\{\text{S}_2\text{CNMe}(\text{C}_3\text{H}_2\text{NS})\}]\cdot\text{CH}_2\text{Cl}_2$ (2)

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|-------|--------------|-------------|--------------|-------|-------------|------------|-------------|
| Re(1) | -0.073 19(2) | 0.770 85(2) | 0.125 26(3) | C(10) | -0.091 8(3) | 0.624 4(3) | 0.605 6(5) |
| P(1) | -0.002 3(1) | 0.717 2(1) | 0.287 8(2) | C(11) | -0.038 9(3) | 0.589 1(3) | 0.571 2(5) |
| P(2) | -0.140 5(1) | 0.817 7(1) | -0.047 5(2) | C(12) | -0.012 6(3) | 0.615 6(3) | 0.473 9(5) |
| S(1) | -0.032 6(1) | 0.687 9(1) | -0.025 3(2) | C(7) | -0.039 3(3) | 0.677 3(3) | 0.411 1(5) |
| S(2) | 0.026 1(1) | 0.823 7(1) | 0.062 0(2) | C(14) | 0.050 2(2) | 0.854 1(3) | 0.370 4(5) |
| S(3) | 0.125 3(2) | 0.879 3(3) | -0.086 8(4) | C(15) | 0.091 2(2) | 0.899 3(3) | 0.445 2(5) |
| C(37) | -0.138 1(4) | 0.709 1(6) | 0.164 9(8) | C(16) | 0.139 0(2) | 0.867 0(3) | 0.524 4(5) |
| C(38) | -0.096 3(4) | 0.852 2(6) | 0.216 2(10) | C(17) | 0.145 9(2) | 0.789 3(3) | 0.528 8(5) |
| O(1) | -0.176 4(4) | 0.667 8(5) | 0.191 1(7) | C(18) | 0.105 0(2) | 0.744 1(3) | 0.454 0(5) |
| O(2) | -0.110 4(4) | 0.902 8(5) | 0.270 2(8) | C(13) | 0.057 1(2) | 0.776 5(3) | 0.374 8(5) |
| N(1) | 0.070 7(4) | 0.739 0(6) | -0.104 5(7) | C(20) | -0.076 8(3) | 0.833 0(3) | -0.244 8(6) |
| N(2) | 0.175 1(5) | 0.754 6(10) | -0.140 9(10) | C(21) | -0.035 6(3) | 0.869 0(3) | -0.311 3(6) |
| C(39) | 0.026 7(4) | 0.749 8(5) | -0.031 4(8) | C(22) | -0.013 9(3) | 0.941 0(3) | -0.280 7(6) |
| C(40) | 0.068 0(6) | 0.669 6(9) | -0.177 4(12) | C(23) | -0.033 4(3) | 0.976 9(3) | -0.183 6(6) |
| C(41) | 0.122 0(5) | 0.785 6(9) | -0.111 1(8) | C(24) | -0.074 6(3) | 0.940 8(3) | -0.117 2(6) |
| C(42) | 0.199 8(12) | 0.882 2(18) | -0.125 2(18) | C(19) | -0.096 3(3) | 0.868 9(3) | -0.147 8(6) |
| C(43) | 0.218 4(9) | 0.812 7(21) | -0.148 8(18) | C(26) | -0.238 9(3) | 0.861 9(3) | 0.072 5(5) |
| C(44) | 0.242 4(8) | 0.084 8(12) | 0.599 5(14) | C(27) | -0.292 6(3) | 0.902 6(3) | 0.090 9(5) |
| Cl(1) | 0.289 4(2) | 0.001 9(3) | 0.616 6(4) | C(28) | -0.313 1(3) | 0.962 1(3) | 0.016 5(5) |
| Cl(2) | 0.192 8(2) | 0.078 7(4) | 0.464 4(5) | C(29) | -0.279 9(3) | 0.980 8(3) | -0.076 3(5) |
| C(2) | 0.008 7(2) | 0.572 5(3) | 0.207 0(6) | C(30) | -0.226 3(3) | 0.940 1(3) | -0.094 7(5) |
| C(3) | 0.037 7(2) | 0.515 4(3) | 0.150 6(6) | C(25) | -0.205 8(3) | 0.880 6(3) | -0.020 3(5) |
| C(4) | 0.099 1(2) | 0.525 0(3) | 0.124 0(6) | C(32) | -0.193 6(3) | 0.675 3(3) | -0.107 0(5) |
| C(5) | 0.131 6(2) | 0.591 5(3) | 0.153 7(6) | C(33) | -0.235 4(3) | 0.626 6(3) | -0.173 4(5) |
| C(6) | 0.102 6(2) | 0.648 6(3) | 0.210 1(6) | C(34) | -0.272 0(3) | 0.651 8(3) | -0.276 0(5) |
| C(1) | 0.041 2(2) | 0.639 0(3) | 0.236 8(6) | C(35) | -0.266 9(3) | 0.725 8(3) | -0.312 3(5) |
| C(8) | -0.092 3(3) | 0.712 5(3) | 0.445 6(5) | C(36) | -0.225 1(3) | 0.774 6(3) | -0.245 9(5) |
| C(9) | -0.118 5(3) | 0.686 1(3) | 0.542 8(5) | C(31) | -0.188 4(3) | 0.749 3(3) | -0.143 3(5) |

(masked by the aryl protons) 6.75 (1 H, d, CH), 3.05 (3 H, s, CH₃).

X-Ray Structure Determination.—Crystal fragments of maximum dimension 0.2 mm were selected and used for the measurement of intensities. Data collection was carried out on a Philips diffractometer with a graphite monochromator and Mo-K_α radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data. For (1). C₄₉H₄₀N₃O₂P₂ReS₂·CH₂Cl₂, *M* = 1 116, triclinic, space group *P* $\bar{1}$, *a* = 15.058(6), *b* = 14.305(6), *c* = 12.371(6) Å, α = 108.51(3), β = 75.16(3), γ = 104.91(3)°, *U* = 2 397 Å³, *Z* = 2, *D*_c = 1.52 g cm⁻³, $\lambda(\text{Mo-K}\alpha)$ = 0.7107 Å, $\mu(\text{Mo-K}\alpha)$ = 29.8 cm⁻¹.

For (2). C₄₃H₃₅N₂O₂P₂ReS₃·CH₂Cl₂, *M* = 1 040, monoclinic, space group *P*2₁/*n*, *a* = 21.305(5), *b* = 17.873(5), *c* = 11.455(7) Å, β = 97.81(3)°, *U* = 4 322 Å³, *Z* = 4, *D*_c = 1.59 g cm⁻³, $\lambda(\text{Mo-K}\alpha)$ = 0.7107 Å, $\mu(\text{Mo-K}\alpha)$ = 33.3 cm⁻¹.

Intensities were measured using the θ – 2θ scan method, with a scan speed of 2° min⁻¹ between 2 and 25°, yielding 8 791 independent reflections for (1), 6 369 of which were significantly above background [*I* > 3 σ (*I*)], and 6 925 independent reflections for (2), 5 749 of which were above background. After subtracting the background, the data were corrected for Lorentz polarization factors and for absorption.¹³ Two standard reflections measured periodically were constant within counting statistics. Solution of the structures was achieved by the heavy-atom method through Patterson and Fourier maps. Refinement of scale-factor, positional, and thermal parameters converged to give the final conventional agreement index *R* of 0.055 for (1) and 0.052 for (2). The structures were refined by full-matrix least squares, minimizing the function $\sum w(\Delta F)^2$ with *w* = 1. The phenyl groups were refined as rigid bodies (C–C 1.395, C–H 1.08 Å) with fixed isotropic thermal parameters for the H atoms (*U* 0.07 Å²). In both compounds the asymmetric unit of

the cell also contains a molecule of CH₂Cl₂ present as a clathrate solvent. In (1) this molecule is disordered with the chlorine (and therefore the hydrogen) atoms statistically distributed in two or more positions. After several attempts to interpret this molecule, we introduced the Cl atoms in geometrically compatible positions with appropriate occupancies and this depressed the *R* factor of ca. 0.5 units. However, some small residuals of electron density in the final Fourier difference map seem to indicate that the Cl atoms of this molecule are more disordered than assumed by our model. Scattering factors for Re were from ref. 14, and those for the other atoms from ref. 15. The rhenium scattering factor was corrected for anomalous dispersion with constant average values $\Delta f' = -1.598$ and $\Delta f'' = 7.232$ for the real and imaginary components. All calculations were done using the SHELX program system.¹⁶ Final atomic co-ordinates for the compounds are listed in Tables 3 and 4. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond parameters.

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