Reactivity of Rhenium(I) Pseudo-allyl Complexes with Heterocumulenes such as RNCS (R = Me or Ph, *p*-MeC_6H_4) and PhNCO. Part 1. Crystal Structure Determination of Two Isostructural Monothio- and Dithio-carbamate Rhenium(I) Complexes co-crystallized as $[Re(CO)_2(PPh_3)_2\{S{=}C(NHPh){-}S\}]\cdot[Re(CO)_2(PPh_3)_2\{O{-}C(NHPh){=}S\}]$†

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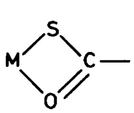
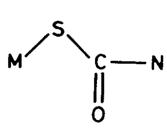
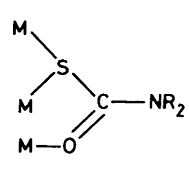
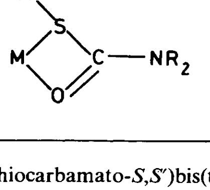
The compounds $[Re(CO)_2(PPh_3)_2(O\cdots CH\cdots NC_6H_4Me\text{-}p)]$ and $[Re(CO)_2(PPh_3)_2(amt)]$ [amt = anion of 2-(aminomethyl)thiazole] react with an excess of PhNCO under non-anhydrous conditions to give the displacement of the starting chelate ligand and the formation of the carbamate complex $[Re(CO)_2(PPh_3)_2\{O\cdots C(NHPh)\cdots O\}]$. When the reaction is carried out under the same conditions with an excess of RNCS (R = Ph or *p*-MeC_6H_4) the monothio- and dithio-carbamate complexes $[Re(CO)_2(PPh_3)_2\{O{-}C(NHR){=}S\}]$ (**1**) and $[Re(CO)_2(PPh_3)_2\{S{=}C(NHR){-}S\}]$ (**2**) are obtained. The formation of complexes (**2**) proceeds *via* the intermediate formation of (**1**). A mixture of complexes (**1b**) and (**2b**) (R = Ph) gives rise to a crystallized compound, which *X*-ray analysis has allowed to be formulated as $[Re(CO)_2(PPh_3)_2\{SC(NHPh)S\}]\cdot[Re(CO)_2(PPh_3)_2\{OC(NHPh)S\}]$ where discrete molecules of two isostructural rhenium complexes are co-crystallized in the monoclinic cell, of space group $P2_1$, with $a = 9.314(6)$, $b = 22.976(4)$, $c = 18.662(5)$ Å, and $\beta = 91.01(3)°$. In both molecules the Re is six-co-ordinate in a distorted octahedral environment with *trans* PPh_3 groups, *cis* CO groups, and one bidentate ligand. Distances in the co-ordination sphere are: Re–P 2.42 (mean), Re–C 1.90 (mean), Re–S 2.52 (mean), and Re–O 2.37 Å. The ligand moieties are essentially planar in both complexes.

In contrast to the extensive literature on the preparation and characterization of dithiocarbamate metal complexes, little has been reported on the co-ordination chemistry of monothiocarbamate ligands. The properties of this class of ligands and complexes differ greatly from those of the corresponding dithiocarbamates and promise to provide an equally rich chemistry. Structural studies[1] show that there are at least four bonding modes for monothiocarbamate ligands as shown below. The most common synthetic procedure for these ligands involves the treatment of carbonyl sulphide, OCS, with a secondary amine to provide an ammonium salt.[2–4] Most of the complexes reported up to now have been prepared by the metathetical reaction of a monothiocarbamate salt with a transition-metal compound. All involve ligands of the type $R_2NC(=O)S^-$ ($R \neq H$).[1]









As a continuation of our studies on the synthesis and reactivity of pseudo-allyl rhenium[5] and technetium[6] complexes, we have conducted investigations on the reactions of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ and $[Re(CO)_2(PPh_3)_2(amt)]$ [amt = anion of 2-(aminomethyl)thiazole] with heterocumulenes such as RNCS (R = Me, Ph, or *p*-MeC_6H_4) and PhNCO. The present report is concerned with the isolation of carbamate and monothiocarbamate complexes where the ligands involved, $PhNHCO_2^-$ and $RNHCOS^-$ (R = H, Ph, or *p*-MeC_6H_4), are obtained by direct reaction of the starting material with PhNCO and RNCS respectively. The monothiocarbamate products (R = Ph or *p*-MeC_6H_4) react further with RNCS giving the dithiocarbamate derivatives.

Results and Discussion

The compounds $[Re(CO)_2(PPh_3)_2(O\cdots CH\cdots NC_6H_4Me\text{-}p)]$ and $[Re(CO)_2(PPh_3)_2(amt)]$ react with an excess of RNCS (R = Ph or *p*-MeC_6H_4) in wet benzene at room temperature giving a pale yellow solution from which the compounds $[Re(CO)_2(PPh_3)_2\{O{-}C(NHR){=}S\}]$ [R = Ph (**1b**) or *p*-MeC_6H_4 (**1c**)] and $[Re(CO)_2(PPh_3)_2\{S{=}C(NHR){-}S\}]$ [R = Ph (**2b**) or *p*-MeC_6H_4 (**2c**)] were obtained in yields of 70—75 and 10—15%, respectively. On the other hand, when the reaction is carried out at reflux temperature the complexes (**2**) are obtained as main products. The monothiocarbamate complexes react further with RNCS giving the dithiocarbamate derivatives. The

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† Dicarbonyl(phenyldithiocarbamato-*S,S'*)bis(triphenylphosphine)rhenium(I)–dicarbonyl(phenylthiocarbamato-*O,S*)bis(triphenylphosphine)rhenium(I) (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 1. Spectroscopic data

	I.r. (Nujol)/cm^{-1}				^{1}H n.m.r. ($CDCl_3$) (δ)	
Compound	ν(C=O)	ν(NH)	ν(C=N)	ν(L)*	$MeC_6\mathit{H}_4$	$\mathit{Me}C_6H_4$
(**1a**) $[Re(CO)_2(PPh_3)_2\{OC(NH_2)S\}]$	1 920, 1 825	3 380	1 555	1 340		
(**1b**) $[Re(CO)_2(PPh_3)_2\{OC(NHPh)S\}]$	1 925, 1 835	3 300	1 520	1 310, 1 230		
(**1c**) $[Re(CO)_2(PPh_3)_2\{OC(NHC_6H_4Me\text{-}p)S\}]$	1 920, 1 825	3 350	1 535	1 330	6.77 (m), 6.30 (m)	2.22(s)
(**2b**) $[Re(CO)_2(PPh_3)_2\{SC(NHPh)S\}]$	1 910, 1 830	3 330	1 520	1 330		
(**2c**) $[Re(CO)_2(PPh_3)_2\{SC(NHC_6H_4Me\text{-}p)S\}]$	1 915, 1 840	3 320	1 510	1 345	6.87 (m), 6.52 (m)	2.22 (s)
(**3**) $[Re(CO)_2(PPh_3)_2\{OC(NHPh)O\}]$	1 910, 1 830	3 410	1 505	1 560		

* Other bands of the chelate ligand.

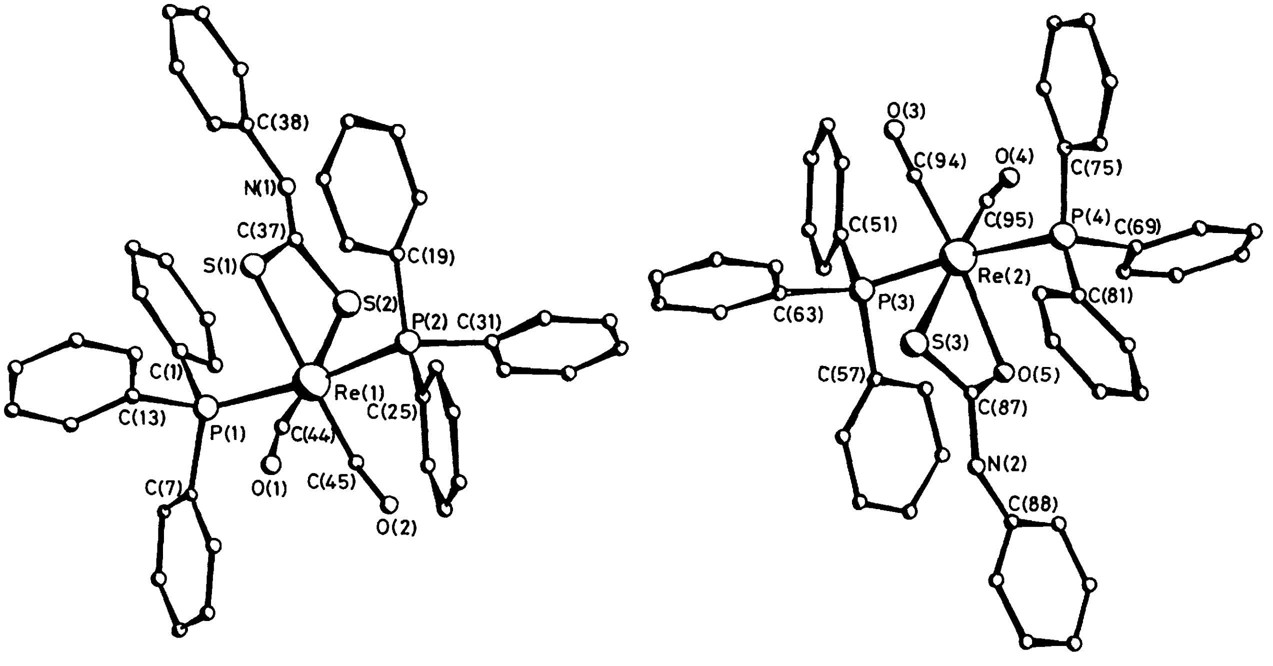

Figure. Crystal structure of co-crystallized $[Re(CO)_2(PPh_3)_2\{S{=}C(NHPh){-}S\}]\cdot[Re(CO)_2(PPh_3)_2\{O{-}C(NHPh){=}S\}]$

complexes, separated by column chromatography using CH_2Cl_2–n-hexane (1:1) as eluant, have been characterized by elemental analysis and i.r. and ^{1}H n.m.r. spectra (Table 1).

The i.r. spectra show the phosphine band at *ca.* 1 090 cm^{-1} and two strong bands for the two *cis* terminal carbonyls in the ranges 1 925—1 910 and 1 840—1 825 cm^{-1}. For both monothio- and dithio-carbamate derivatives the C–N stretching absorption is in the region 1 560—1 500 cm^{-1}, indicating partial double-bond character of the C–N groups as a consequence of the chelating behaviour of the ligands.[1,7,8] The co-ordinated ligands show ν(NH) values in the range 3 350—3 300 cm^{-1}. No significant bands are observed in the ν(CS) region (1 000—900 cm^{-1}), while a band of medium–weak intensity is present in the range 1 345—1 310 cm^{-1}, probably related to vibrations of the chelate ligands.

The reaction with MeNCS carried out at room temperature, under the same experimental conditions, leads to the formation of a white precipitate whose i.r. analysis shows the presence of ν(NH) at 3 380 cm^{-1} and ν(CN) at 1 555 cm^{-1} in addition to absorption bands due to CO and phosphine groups, while the ^{1}H n.m.r. spectrum does not reveal a methyl resonance. These findings, together with the elemental analysis, allow us to formulate the compound as $[Re(CO)_2(PPh_3)_2\{OC(NH_2)S\}]$ (**1a**).

From the reaction of the complex $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ with an excess of PhNCO, the carbamate derivative $[Re(CO)_2(PPh_3)_2\{O{\cdots}C(NHPh){\cdots}O\}]$ (**3**) was obtained. Our formulation of this complex is supported by i.r. evidence. The two strong terminal carbonyl stretching frequencies, which lie in the usual region, suggest a *cis* arrangement of the carbonyl groups. Two bands are present at 1 560 and 1 505 cm^{-1}; the lower-frequency band could be assigned to the CO_2 group of the carbamate ligand,[7] while the higher one is assigned to the CN group; moreover the ν(NH) frequency is present in the expected region at 3 410 cm^{-1}.

These reactions with heterocumulene molecules such as PhNCO and RNCS probably proceed *via* the intermediate formation of the corresponding carbamic or monothiocarbamic acids and subsequent electrophilic attack of the acid proton on the lone pair of a nitrogen atom co-ordinated to the metal. This seems to exclude a previously reported[9] reaction of the starting complexes with the heterocumulene ligands giving rise to a formal insertion into the M–N bond; these rhenium(I) insertion products are obtained when the reactions are carried out under anhydrous conditions.[10] The reactions were carried out in wet solvent thus allowing the isolation of monothiocarbamate complexes of rhenium(I) which, to our knowledge, are the first examples of monothiocarbamate derivatives of a transition

Table 2. Bond lengths (Å)

(2b)		(1b)	
Re(1)–P(1)	2.403(4)	Re(2)–P(3)	2.397(6)
Re(1)–P(2)	2.411(5)	Re(2)–P(4)	2.449(5)
Re(1)–S(1)	2.512(5)	Re(2)–O(5)	2.37(1)
Re(1)–S(2)	2.525(5)	Re(2)–S(3)	2.529(5)
Re(1)–C(44)	1.90(1)	Re(2)–C(94)	1.91(2)
Re(1)–C(45)	1.87(2)	Re(2)–C(95)	1.93(3)
C(44)–O(1)	1.17(2)	C(94)–O(3)	1.13(2)
C(45)–O(2)	1.16(2)	C(95)–O(4)	1.13(3)
S(1)–C(37)	1.65(2)	O(5)–C(87)	1.49(2)
S(2)–C(37)	1.79(2)	S(3)–C(87)	1.65(2)
C(37)–N(1)	1.36(3)	C(87)–N(2)	1.41(3)
N(1)–C(38)	1.45(2)	N(2)–C(88)	1.42(2)
P(1)–C(1)	1.92(2)	P(3)–C(51)	1.89(2)
P(1)–C(7)	1.85(2)	P(3)–C(57)	1.88(1)
P(1)–C(13)	1.87(1)	P(3)–C(63)	1.85(2)
P(2)–C(19)	1.80(2)	P(4)–C(69)	1.86(2)
P(2)–C(25)	1.82(1)	P(4)–C(75)	1.84(2)
P(2)–C(31)	1.81(1)	P(4)–C(81)	1.78(2)

Table 3. Bond angles (°)

(2b)		(1b)	
S(1)–Re(1)–S(2)	70.9(2)	O(5)–Re(2)–S(3)	66.2(3)
S(1)–Re(1)–C(44)	100.1(5)	O(5)–Re(2)–C(95)	109.0(7)
S(2)–Re(1)–C(45)	97.3(5)	S(3)–Re(2)–C(94)	96.9(6)
C(44)–Re(1)–C(45)	92.0(1)	C(94)–Re(2)–C(95)	88.2(9)
P(1)–Re(1)–P(2)	171.1(2)	P(3)–Re(2)–P(4)	172.2(2)
Re(1)–C(44)–O(1)	168.0(2)	Re(2)–C(95)–O(4)	169.0(2)
Re(1)–C(45)–O(2)	170.0(2)	Re(2)–C(94)–O(3)	173.0(2)
Re(1)–S(1)–C(37)	87.8(6)	Re(2)–O(5)–C(87)	91.1(9)
Re(1)–S(2)–C(37)	84.6(6)	Re(2)–S(3)–C(87)	82.4(7)
S(1)–C(37)–S(2)	116.0(1)	O(5)–C(87)–S(3)	117.0(1)
S(1)–C(37)–N(1)	127.0(1)	O(5)–C(87)–N(2)	120.0(2)
S(2)–C(37)–N(1)	114.0(2)	S(3)–C(87)–N(2)	118.0(2)
C(37)–N(1)–C(38)	118.0(1)	C(87)–N(2)–C(88)	137.0(2)
Re(1)–P(1)–C(1)	118.1(6)	Re(2)–P(3)–C(51)	116.7(5)
Re(1)–P(1)–C(7)	119.4(4)	Re(2)–P(3)–C(57)	108.9(5)
Re(1)–P(1)–C(13)	114.7(4)	Re(2)–P(3)–C(63)	121.7(5)
Re(1)–P(2)–C(19)	110.3(6)	Re(2)–P(4)–C(69)	115.2(6)
Re(1)–P(2)–C(25)	113.5(4)	Re(2)–P(4)–C(75)	109.5(6)
Re(1)–P(2)–C(31)	121.6(5)	Re(2)–P(4)–C(81)	113.0(5)

metal having ligands with a protonated nitrogen in the co-ordination sphere.[1] The subsequent incorporation of sulphur, required for the formation of the dithiocarbamate compounds, arises plausibly by abstraction from RNCS (R = Ph or *p*-MeC_6H_4) and the consequent evolution of RNCO.

X-Ray Structure of $[Re(CO)_2(PPh_3)_2\{S{=}C(NHPh)\text{–}S\}]\cdot[Re(CO)_2(PPh_3)_2\{O\text{–}C(NHPh){=}S\}]$.—Surprisingly, a mixture of the two complexes (**1b**) and (**2b**) treated with CH_2Cl_2–EtOH gives rise to a crystallized compound which, as shown in the Figure, consists of co-crystallized, discrete molecules of $[Re(CO)_2(PPh_3)_2\{SC(NHPh)S\}]$ and $[Re(CO)_2(PPh_3)_2\{OC(NHPh)S\}]$. The Figure shows the conformation of the molecules and the numbering scheme used throughout this paper. Bond distances and angles are listed in Tables 2 and 3, and atomic co-ordinates in Table 4.

In both molecules the Re atom is in a distorted octahedral environment with *trans* PPh_3 groups, *cis* CO groups, and one chelate ligand. Distortion from the idealized geometry is mainly due to the geometry of the chelate ligands which subtend angles of *ca.* 70° at the metal. Deviations of 8—9° from linearity for the axial substituents are also observed. Mean-plane calculations show that the equatorially bonded atoms (2 S and 2 C) or (S, O, and 2 C) are approximately coplanar, being alternatively displaced by $\pm(0.01\text{—}0.02)$ Å from the base plane. The chelate ligands as a whole are also roughly planar with dihedral angles of a few degrees between the phenyl group and the rest of the ligand. Since the two molecules differ only in the presence of one oxygen instead of a suphur atom in the bidentate ligand, most structural details are fully comparable so that the mean values obtained from the two independent determinations can be considered with sufficient confidence. Thus, the *trans* Re^I–P and the *cis* Re^I–C bond distances have mean values of 2.415 and 1.90 Å respectively, which agree well with 2.420 and 1.90 Å, the average for a number of previous determinations.[5,11,12]

As far as the bidentate ligands are concerned, it is noticeable that both Re–S and Re–O distances are generally longer than expected on the basis of the sum of the covalent radii and appear to be essentially determined by the geometrical constraints of the chelating groups. A closer approach of O and S to the metal atom would indeed result in more conventional Re–S and Re–O bond distances, but would also require narrowing of the Re–S–N or Re–O–N angles, which is highly unlikely considering that the actual values are already less than 90°. On the other hand the Re–S bond distances, which lie in the range 2.51—2.53 Å, mean 2.52 Å, compare very favourably with the mean of 2.515 Å found in $[Re(CO)_2(PPh_3)_2(S_2CH)]$,[12] a compound with the same basic structure.

The two S–C bonds in (**2b**) differ significantly while the S(2)–C(37) bond length of 1.79(2) Å agrees well with the value predicted for a single C(*sp*^{2})–S bond.[13] The S(1)–C(37) distance of 1.65(2) Å allows us to attribute strong double-bond character to this bond, and this differs from what has been observed in other dithiocarbamate complexes where the structural data show a delocalized negative charge over the chelate ring.[14] It is noteworthy that the Re–S distances remain apparently unaffected by the fact that the negative charge of the ligand is localized on S(2), confirming the idea that other factors are prevalent in determining them. Likewise, the S(3)–C(87) bond of 1.65(2) in (**1b**), can be considered as a double bond, whereas O(5)–C(87) of 1.49(2) Å is normal for a single covalent bond, suggesting that the more electronegative oxygen atom is negatively charged, as expected. This is in contrast with the structural data reported for other monothiocarbamate complexes[1] where the negative charge resides on the sulphur atom, suggesting a considerable 'sulphide' character on this one. The mean C–N bond distance, *ca.* 1.38 Å, is comparable to the corresponding value in other monothio- and dithio-carbamate complexes[1,14] and represents a partial multiple-bond character. Other structural details are expected and need no comment.

Experimental

Solvents, when necessary, were purified and dried before use. The starting compounds $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ and $[Re(CO)_2(PPh_3)_2(amt)]$ were prepared following the literature methods.[5] The compounds RNCS and PhNCO were commercially available. Other materials were reagent grade. I.r. and ^1H n.m.r. spectra were recorded on Perkin-Elmer 577 and Bruker WP 80-MHz spectrometers, respectively. Elemental analyses were performed on a Carlo Erba elemental analyser, model 1106.

Synthesis of the Complexes.—$[Re(CO)_2(PPh_3)_2\{OC(NH_2)S\}]$ (**1a**). A large excess of the ligand MeNCS was added to a benzene solution (25 cm^3) of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ or $[Re(CO)_2(PPh_3)_2(amt)]$ (0.166 mmol). After 50 h at room temperature the product was obtained as a white precipitate. It was removed by filtration, washed with EtOH and Et_2O, and reprecipitated from CH_2Cl_2–EtOH (7:3

Table 4. Atomic co-ordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	0.738 21(6)	0.750 00(0)	0.157 18(3)	Re(2)	0.260 92(8)	0.255 89(4)	0.342 23(4)
P(1)	0.767 03(46)	0.852 28(19)	0.180 22(25)	P(3)	0.287 34(57)	0.359 45(24)	0.350 43(30)
P(2)	0.705 97(46)	0.645 90(20)	0.153 99(30)	P(4)	0.230 65(57)	0.152 08(23)	0.316 26(30)
C(44)	0.541 25(130)	0.755 72(87)	0.181 68(93)	C(94)	0.305 34(223)	0.244 80(86)	0.444 34(104)
O(1)	0.415 53(121)	0.759 04(80)	0.183 87(82)	O(3)	0.322 72(161)	0.233 43(60)	0.500 17(79)
C(45)	0.695 27(171)	0.760 45(85)	0.059 52(109)	C(95)	0.463 04(289)	0.248 13(107)	0.324 11(108)
O(2)	0.684 65(166)	0.761 79(69)	−0.002 39(69)	O(4)	0.574 95(149)	0.244 59(72)	0.302 07(92)
S(1)	0.851 94(48)	0.746 64(26)	0.280 18(25)	O(5)	0.136 88(109)	0.266 29(45)	0.228 99(65)
S(2)	1.006 24(52)	0.737 62(29)	0.145 76(32)	S(3)	−0.002 93(52)	0.278 74(22)	0.355 46(28)
N(1)	1.138 16(159)	0.735 92(82)	0.266 10(92)	N(2)	−0.129 17(197)	0.281 76(86)	0.225 62(102)
C(37)	1.006 54(200)	0.733 28(66)	0.241 39(81)	C(87)	−0.007 57(194)	0.267 38(83)	0.270 69(107)
C(39)	1.296 06(152)	0.732 43(75)	0.372 46(81)	C(89)	−0.323 35(169)	0.297 61(87)	0.144 91(93)
C(40)	1.329 07(152)	0.730 41(75)	0.445 62(81)	C(90)	−0.377 17(169)	0.302 10(87)	0.074 90(93)
C(41)	1.219 09(152)	0.727 36(75)	0.495 26(81)	C(91)	−0.288 33(169)	0.290 42(87)	0.017 24(93)
C(42)	1.076 11(152)	0.726 34(75)	0.471 74(81)	C(92)	−0.145 67(169)	0.274 25(87)	0.029 59(93)
C(43)	1.043 10(152)	0.728 36(75)	0.398 58(81)	C(93)	−0.091 85(169)	0.269 76(87)	0.099 61(93)
C(38)	1.153 08(152)	0.731 41(75)	0.348 94(81)	C(88)	−0.180 69(169)	0.281 44(87)	0.157 27(93)
C(2)	1.011 72(181)	0.887 55(80)	0.268 06(71)	C(52)	0.574 65(179)	0.363 14(65)	0.410 36(88)
C(3)	1.157 76(181)	0.898 09(80)	0.279 77(71)	C(53)	0.714 35(179)	0.384 75(65)	0.416 07(88)
C(4)	1.249 56(181)	0.902 38(80)	0.221 75(71)	C(54)	0.756 07(179)	0.431 57(65)	0.373 65(88)
C(5)	1.195 31(181)	0.896 14(80)	0.152 01(71)	C(55)	0.658 10(179)	0.456 79(65)	0.325 52(88)
C(6)	1.049 27(181)	0.885 60(80)	0.140 31(71)	C(56)	0.518 40(179)	0.435 18(65)	0.319 81(88)
C(1)	0.957 47(181)	0.881 31(80)	0.198 33(71)	C(51)	0.476 67(179)	0.388 35(65)	0.362 23(88)
C(8)	0.568 36(99)	0.891 25(37)	0.082 38(55)	C(58)	0.296 60(118)	0.381 36(61)	0.201 66(72)
C(9)	0.508 09(99)	0.926 16(37)	0.028 61(55)	C(59)	0.242 07(118)	0.400 18(61)	0.135 53(72)
C(10)	0.581 01(99)	0.975 49(37)	0.005 26(55)	C(60)	0.112 82(118)	0.430 81(61)	0.131 87(72)
C(11)	0.714 20(99)	0.989 90(37)	0.035 69(55)	C(61)	0.038 11(118)	0.442 61(61)	0.194 35(72)
C(12)	0.774 47(99)	0.954 98(37)	0.089 46(55)	C(62)	0.092 64(118)	0.423 78(61)	0.260 49(72)
C(7)	0.701 55(99)	0.905 65(37)	0.112 81(55)	C(57)	0.221 89(118)	0.393 16(61)	0.264 14(72)
C(14)	0.652 67(126)	0.939 20(42)	0.270 16(56)	C(64)	0.208 61(168)	0.462 38(59)	0.430 07(76)
C(15)	0.593 25(126)	0.960 34(42)	0.333 12(56)	C(65)	0.151 48(168)	0.488 73(59)	0.490 58(76)
C(16)	0.552 87(126)	0.921 75(42)	0.386 84(56)	C(66)	0.085 88(168)	0.454 84(59)	0.542 68(76)
C(17)	0.571 90(126)	0.862 01(42)	0.377 59(56)	C(67)	0.077 41(168)	0.394 60(59)	0.534 27(76)
C(18)	0.631 33(126)	0.840 87(42)	0.314 63(56)	C(68)	0.134 54(168)	0.368 25(59)	0.473 76(76)
C(13)	0.671 71(126)	0.879 46(42)	0.260 91(56)	C(63)	0.200 14(168)	0.402 14(59)	0.421 66(76)
C(20)	0.910 40(161)	0.591 18(78)	0.243 58(82)	C(70)	0.335 37(223)	0.067 46(74)	0.215 45(111)
C(21)	0.966 70(161)	0.578 93(78)	0.311 69(82)	C(71)	0.416 38(223)	0.051 92(74)	0.156 27(111)
C(22)	0.884 47(161)	0.589 19(78)	0.372 15(82)	C(72)	0.481 03(223)	0.094 90(74)	0.115 05(111)
C(23)	0.745 94(161)	0.611 69(78)	0.364 51(82)	C(73)	0.464 67(223)	0.153 43(74)	0.133 01(111)
C(24)	0.689 63(161)	0.623 93(78)	0.296 40(82)	C(74)	0.383 66(223)	0.168 98(74)	0.192 19(111)
C(19)	0.771 86(161)	0.613 68(78)	0.235 94(82)	C(69)	0.319 01(223)	0.126 00(74)	0.233 41(111)
C(26)	0.445 22(114)	0.649 19(47)	0.085 20(61)	C(76)	0.434 02(186)	0.117 74(71)	0.430 73(108)
C(27)	0.304 86(114)	0.632 00(47)	0.068 69(61)	C(77)	0.478 34(186)	0.076 29(71)	0.481 06(108)
C(28)	0.238 60(114)	0.589 29(47)	0.109 70(61)	C(78)	0.397 18(186)	0.025 99(71)	0.490 95(108)
C(29)	0.312 72(114)	0.563 78(47)	0.167 22(61)	C(79)	0.271 68(186)	0.017 14(71)	0.450 50(108)
C(30)	0.453 08(114)	0.580 98(47)	0.183 73(61)	C(80)	0.227 36(186)	0.058 59(71)	0.400 17(108)
C(25)	0.519 34(114)	0.623 69(47)	0.142 72(61)	C(75)	0.308 52(186)	0.108 89(71)	0.390 28(108)
C(32)	0.860 37(154)	0.627 35(42)	0.029 34(76)	C(82)	0.000 83(128)	0.114 99(64)	0.232 67(57)
C(33)	0.915 25(154)	0.593 03(42)	−0.025 43(76)	C(83)	−0.143 46(128)	0.101 19(64)	0.220 66(57)
C(34)	0.896 80(154)	0.532 80(42)	−0.024 01(76)	C(84)	−0.240 11(128)	0.104 42(64)	0.276 78(57)
C(35)	0.823 47(154)	0.506 87(42)	0.032 17(76)	C(85)	−0.192 48(128)	0.121 44(64)	0.344 90(57)
C(36)	0.768 59(154)	0.541 18(42)	0.086 94(76)	C(86)	−0.048 20(128)	0.135 23(64)	0.356 91(57)
C(31)	0.787 04(154)	0.601 42(42)	0.085 53(76)	C(81)	0.048 46(128)	0.132 01(64)	0.300 79(57)

v/v) (80%), m.p. 205 °C, white (Found: C, 53.7: H, 3.8; N, 1.6; S, 3.6. $C_{39}H_{32}NO_3P_2ReS$ requires C, 51.7; H, 3.5; N, 1.5; S, 3.5%).

$[Re(CO)_2(PPh_3)_2\{OC(NHR)S\}]$ [R = Ph (**1b**) *or* *p*-MeC_6H_4 (**1c**)]. A large excess of the appropriate ligand RNCS (R = Ph or *p*-MeC_6H_4) was added to a benzene solution (40 cm^3) of the starting compound $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ or $[Re(CO)_2(PPh_3)_2(amt)]$ (0.166 mmol). After 50 h at room temperature the mixture was filtered and concentrated *in vacuo*. The resulting precipitate was removed by filtration and washed with EtOH and Et_2O. The products (**1b**) and (**1c**) were separated from the presence of a small amount of the corresponding dithiocarbamate complexes, (**2b**) and (**2c**), by chromatography using a silica-gel plate (2 mm) [CH_2Cl_2–n-hexane (1:1) as eluant]. The complexes were crystallized from CH_2Cl_2–EtOH (7:3 v/v): $[Re(CO)_2(PPh_3)_2\{OC(NHPh)S\}]$ (**1b**) (70%), m.p. 209 °C, pale yellow (Found: C, 58.0; H, 3.9; N, 1.4; S, 3.6. $C_{45}H_{36}NO_3P_2ReS$ requires C, 58.8; H, 3.9; N, 1.5; S, 3.5%); $[Re(CO)_2(PPh_3)_2\{OC(NHC_6H_4Me\text{-}p)S\}]$ (**1c**) (75%), m.p. 202 °C, pale yellow (Found: C, 59.7; H, 4.1; N, 1.4; S, 3.6. $C_{46}H_{38}NO_3P_2ReS$ requires C, 59.2; H, 4.1; N, 1.5; S, 3.4%).

$[Re(CO)_2(PPh_3)_2\{SC(NHR)S\}]$ [R = Ph (**2b**) *or* *p*-MeC_6H_4 (**2c**)]. A large excess of the appropriate ligand RNCS (R = Ph or *p*-MeC_6H_4) was added to a benzene solution (40 cm^3) of the starting compound $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ or $[Re(CO)_2(PPh_3)_2(amt)]$ (0.166 mmol). Upon heating under reflux the solution became yellow. After 3 h the mixture was filtered and the solution was concentrated *in vacuo*. The resulting precipitate was removed by filtration and washed with EtOH and Et_2O. The products (**2b**) and (**2c**) were separated from the small amount of the corresponding monothiocarbamate complex by chromatography as described above: $[Re(CO)_2(PPh_3)_2\{SC(NHPh)S\}]$ (**2b**) (80%), m.p. 196 °C, yellow (Found: C, 57.9; H, 3.6; N, 1.4; S, 6.6. $C_{45}H_{36}NO_2P_2ReS_2$ requires C, 57.8; H, 3.8; N, 1.5; S, 6.8%); $[Re(CO)_2(PPh_3)_2\{SC(NHC_6H_4Me\text{-}p)S\}]$ (**2c**) (85%), m.p. 185 °C, yellow (Found: C, 56.1; H, 4.0; N, 1.6; S, 6.2. $C_{46}H_{38}NO_2P_2ReS_2$ requires C, 58.2; H, 4.0; N, 1.5; S, 6.8%).

$[Re(CO)_2(PPh_3)_2\{OC(NHPh)O\}]$ (**3**). A large excess of PhNCO was added to a benzene solution (40 cm^3) of the starting compound $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ (0.166 mmol). After 2 h at reflux temperature the mixture was filtered and the solution was concentrated *in vacuo* to one third of its original volume. A pale yellow powder was obtained by adding n-heptane. The solid was washed with EtOH and Et_2O and crystallized from CH_2Cl_2–n-hexane (7:3 v/v) (85%), m.p. 198 °C, yellow (Found: C, 58.8; H, 3.9; N, 1.4. $C_{45}H_{36}NO_4P_2Re$ requires C, 59.8; H, 4.0; H, 1.5%).

X-Ray Crystallography.—A crystal of approximate dimensions 0.1 × 0.2 × 0.2 mm was used for the measurement of intensities. Data collection was made on a Philips diffractometer with a graphite monochromator and Mo-K_α radiation (λ = 0.710 69 Å). Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data. $C_{90}H_{72}N_2O_5P_4Re_2S_3$, M = 1 854 (935 + 919), monoclinic, space group $P2_1$ or $P2_1/m$ from the systematic absences $0k0$ for $k = 2n + 1$, the former confirmed by the structure determination, a = 9.314(6), b = 22.976(4), c = 18.662(5) Å, β = 91.01(3)°, U = 3 993 $Å^3$, D_c = 1.54 g cm^{-3}, Z = 2, $F(000)$ = 1 848, μ(Mo-K_α) = 49.3 cm^{-1}.

Intensities were measured by the θ–2θ method, with a scan rate of 2° min^{-1} up to θ = 25°, yielding 8 604 reflections, 5 319 of which were significantly above background $I > 3\sigma(I)$. The recorded intensities were corrected for Lorentz polarization factors and for absorption.[15] Two standard reflections measured periodically were constant within counting statistics. Solution of the structure was achieved by the heavy-atom method through Patterson and Fourier maps.

The value of the density clearly indicated the presence in the unit cell of four molecules, which, in principle, suggested the centrosymmetric space group $P2_1/m$, which has four general positions. However, this choice proved to be inconsistent and the structure was successfully solved by locating two independent molecules in the asymmetric unit of the acentric space group $P2_1$, which has only two equivalent positions. The reason for this became clear later, when the refinement of the structure unambiguously showed that the two independent molecules had a slightly different chemical composition and the entire compound must actually be formulated as $[Re(CO)_2(PPh_3)_2\{SC(NHPh)S\}]\cdot[Re(CO)_2(PPh_3)_2\{OC(NHPh)S\}]$.

Refinement of scale-factor, positional, and thermal parameters converged to the final agreement index R of 0.051, when the largest parameter shift in the last cycle was *ca*. 0.2. The structure was refined by full-matrix least squares, minimizing the function $\Sigma w(\Delta F)^2$ with w = 1. During the refinement the phenyl groups were considered as rigid bodies (C–C 1.395 Å) in order to reduce the number of parameters.

A final Fourier difference map showed no significant residuals apart from some ripples of maximum height 1.8 e $Å^{-3}$ near the positions of the rhenium atoms. Attempts to replace the oxygen atom O(5) of the chelate ligand in $[Re(CO)_2(PPh_3)_2\{OC(NHPh)S\}]$ with a sulphur atom did not vary bond distances, which remained compatible with the dimensions of an oxygen atom, and caused anomalies in the thermal parameters with a contemporaneous increase in the R factor to 0.06, which confirmed the original choice.

Atomic scattering factors for neutral atoms were those from ref. 16. The rhenium scattering factor was corrected for the effects of anomalous dispersion. Calculations were performed using the SHELX program system.[17] Distances and angles are in Tables 2 and 3, final atomic co-ordinates in Table 4.

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