The Chemistry of Heteroallene and Heteroallyl Derivatives of Rhenium. Part 2.[1] Reactivity of $[ReO(OR)Cl_2(PPh_3)_2]$ (R = Me or Et) with RNCS (R = Ph or p-MeC_6H_4). Crystal Structure of the Thiazetidine Rhenium(V) Complex $[ReOCl_2(PPh_3)\{p\text{-}MeC_6H_4N{=}C(OEt){-}S\}]$†

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The complex $[ReO(OR)Cl_2(PPh_3)_2]$ (R = Me or Et) reacts with an excess of RNCS (R = Ph or p-MeC_6H_4) to give the thiazetidine complexes $[ReOCl_2(PPh_3)\{RN{=}C(OR){-}S\}]$ obtained by formal insertion of the heterocumulene molecule into the Re–OR bond. The crystal structure of the complex $[ReOCl_2(PPh_3)\{p\text{-}MeC_6H_4N{=}C(OEt){-}S\}]$ was determined by *X*-ray crystallography. The compound is triclinic, space group $P\bar{1}$ with a = 12.991(5), b = 11.394(5), c = 10.024(5) Å, α = 93.53(3), β = 100.29(3), γ = 77.74(3)°, and Z = 2. The structure was refined to R = 0.035 for 4 626 independent reflections. The Re atom is six-co-ordinate distorted octahedral. The organic ligand is chelated through the nitrogen and sulphur atoms and makes with the metal a roughly planar four-membered ring. Selected bond distances are: Re–O 1.671(4), Re–P 2.488(2), Re–Cl 2.381(2) and 2.437(2), Re–N 2.087(5), and Re–S 2.406(2) Å.

In Part 1 of this series we have described the reactions of RNCS (R = Ph or p-MeC_6H_4) and PhNCO with rhenium(I) carbonyl complexes which gave rise to thiazetidine and oxazetidine complexes of the type $[Re(CO)_2(PPh_3)_2\{RNC(OEt)S\}]$ and $[Re(CO)_2(PPh_3)_2\{PhNC(OEt)O\}]$ respectively.[1] Here we describe the reactions of the rhenium(V) oxo complexes $[ReO(OR)Cl_2(PPh_3)_2]$ (R = Me or Et) with RNCS (R = Ph or p-MeC_6H_4) in order to obtain thiazetidine rhenium compounds with the metal in a higher oxidation state.

Results and Discussion

The reaction of $[ReO(OR)Cl_2(PPh_3)_2]$ (R = Me or Et) with an excess of RNCS (R = Ph or p-MeC_6H_4) in benzene at room temperature for 7—8 h or at reflux temperature for 1—2 h produces the thiazetidine complexes $[ReOCl_2(PPh_3)\{RN{=}C(OR){-}S\}]$ as a consequence of a formal insertion of the ligand into the Re–OR bond of the starting complex. The complex $[ReOCl_2(PPh_3)\{PhN{=}C(OEt){-}S\}]$ can also be obtained by reacting $[ReOCl_3(PPh_3)_2]$ with an excess of the ligand PhNC(OEt)SH at room or reflux temperature.

Information concerning the reaction mechanism can be obtained by carrying out the reaction in the presence of an excess of free PPh_3. No reaction product is obtained when the ethoxy compound $[ReO(OEt)Cl_2(PPh_3)_2]$ is used in the presence of the PhNCS ligand, and only the starting material is recovered. On the contrary, the PPh_3 does not affect the reaction when the PhNC(OEt)SH ligand is present and the pseudoallyl complex is formed. On this basis, the first step in the complex formation using the heteroallene ligand is probably the substitution of a PPh_3 group by a PhNCS molecule co-ordinated to the metal centre *via* the nitrogen atom. Substitution of a PPh_3 ligand by a nitrogen atom has already been observed using Schiff-base ligands (HL). The complex formed, $[ReOCl_3(PPh_3)(HL)]$ (HL = N-methylsalicylideneimine), has the Schiff base co-ordinated as a unidentate ligand through the aldimine nitrogen.[2]

The intermediate product then evolves to the final compound by nucleophilic attack of a lone pair of the ethoxo group on the central carbon of the heteroallene molecule and consequent substitution of the RO^- group on the metal centre by the sulphur atom.

When the reaction is carried out with PhNC(OEt)SH, the first step in the complex formation is now the electrophilic attack of the acid proton on a lone pair of the ethoxo group and subsequent substitution of the negatively charged group by means of the 'mercaptide' sulphur atom of the ionic form of the ligand. The following ring closure through the nitrogen atom now proceeds *via* loss of a phosphine ligand. An excess of free PPh_3 does not inhibit the nitrogen attack because the chelating effect prevails.

The characterization of the complexes was achieved on the basis of elemental analysis, i.r., and ^1H n.m.r. spectra (see Experimental section). The i.r. spectra show the phosphine ν(P–C) band at 1 090 cm^{-1} whereas the Re$\equiv$O stretching frequency appears at 985 cm^{-1}, a higher value than in the starting complex $[ReOCl_3(PPh_3)_2]$ [ν(Re$\equiv$O) 968 cm^{-1}] or $[ReO(OR)Cl_2(PPh_3)_2]$ [ν(Re$\equiv$O) 949 cm^{-1}].[3] This increase in ν(Re$\equiv$O) is observed in analogous dithiocarbamate complexes.[4] The ν(C$\cdots$N) frequency is present at *ca.* 1 510 cm^{-1} and the occurrence of the band in this range is usually considered as evidence of the partial double-bond character of the C–N group,[5] while the bands present in the 1 200—1 300 cm^{-1} region seem to be related to vibrations arising from the chelate ligand.

The n.m.r. spectra show the expected signals due to the alkoxo groups and the heterocumulene moiety. The spectroscopic and analytical data suggest the formation of the complexes $[ReOCl_2(PPh_3)\{RN{=}C(OR){-}S\}]$ (**1**).

Structural studies carried out on the complex $[ReOCl_2(PPh_3)\{p\text{-}MeC_6H_4N{=}C(OEt){-}S\}]$ (**2**) (see Figure) show the rhenium atom in a distorted octahedral co-ordination with the chelate ligand in the equatorial plane and a Cl atom in apical position *trans* to the Re$\equiv$O$_{oxo}$ group. The structure reveals

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† Dichloro[O-ethyl (p-tolylphenylimino)thiocarbonato-SN]oxorhenium(V).

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

Table 1. Bond distances (Å) and angles (°) in (**2**)

Re–O(1)	1.671(4)	Re–S(1)	2.406(2)	P(1)–C(13)	1.826(5)	O(2)–C(20)	1.479(7)
Re–Cl(1)	2.381(2)	Re–P(1)	2.488(2)	C(19)–S(1)	1.735(6)	C(20)–C(21)	1.506(10)
Re–Cl(2)	2.437(2)	P(1)–C(1)	1.825(5)	C(19)–N(1)	1.319(8)	N(1)–C(22)	1.417(6)
Re–N(1)	2.087(5)	P(1)–C(7)	1.820(5)	C(19)–O(2)	1.298(7)	C(25)–C(28)	1.529(9)
Cl(1)–Re–Cl(2)	85.1(1)	Cl(2)–Re–S(1)	84.3(1)	Re–S(1)–C(19)	78.8(2)	Re–N(1)–C(22)	134.0(3)
Cl(1)–Re–P(1)	93.7(1)	Cl(2)–Re–O(1)	169.3(2)	Re–N(1)–C(19)	101.4(4)	C(19)–N(1)–C(22)	124.6(5)
Cl(1)–Re–N(1)	93.4(1)	P(1)–Re–N(1)	166.6(1)	S(1)–C(19)–N(1)	111.5(4)	Re–P(1)–C(7)	111.9(2)
Cl(1)–Re–S(1)	159.1(1)	P(1)–Re–O(1)	87.8(2)	S(1)–C(19)–O(2)	127.1(5)	Re–P(1)–C(13)	109.8(2)
Cl(1)–Re–O(1)	96.5(2)	N(1)–Re–S(1)	68.3(1)	N(1)–C(19)–O(2)	121.3(6)	C(1)–P(1)–C(7)	103.7(2)
Cl(2)–Re–P(1)	81.5(1)	N(1)–Re–O(1)	102.6(2)	C(19)–O(2)–C(20)	119.4(5)	C(1)–P(1)–C(13)	105.4(2)
Cl(2)–Re–N(1)	87.8(2)	S(1)–Re–O(1)	97.2(2)	O(2)–C(20)–C(21)	110.2(6)	C(7)–P(1)–C(13)	105.6(2)

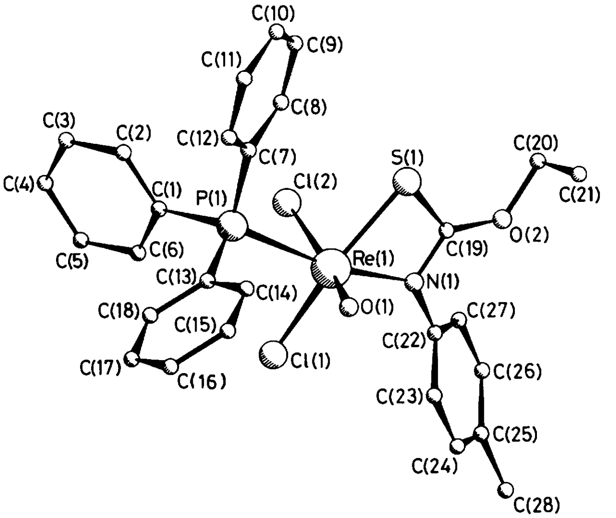

Figure. Crystal structure of [$ReOCl_2(PPh_3)\{p\text{-}MeC_6H_4N{=}C(OEt){-}S\}$] (**2**)

how the charged donor atom (S^-) of the thiazetidine does not take the place of the leaving RO^- group. This situation is in contrast with that observed for analogous complexes in which the chelate ligand is an O^-,N-co-ordinated Schiff base. In these complexes the charged donor atom is always *trans* with respect to the $Re{\equiv}O_{oxo}$ group.[6] This different observed behaviour can be understood by admitting a definite *trans* influence (and therefore a *trans* weakening) caused by the $Re{\equiv}O_{oxo}$ bond, which increases according to the *trans* ligand, in the order $RO^- < Cl^-, Br^- < RN < S^-$ in agreement with the hard acid character of Re^V.[6]

X-Ray Structure of [$ReOCl_2(PPh_3)\{p\text{-}MeC_6H_4N{=}C(OEt){-}S\}$] (**2**).—The molecular structure of the compound is shown in the Figure. The Re atom is six-co-ordinate distorted octahedral, the major asymmetries in bond angles being due to the geometrical constraints of the chelate ligand, which subtends an angle of only 68° at the metal atom, while those in bond lengths are mainly due to the nature of the bonded atoms.

The Re–O(1) distance of 1.671(4) Å (Table 1) indicates the presence of a triple bond and compares well with the values found in other Re^V oxo complexes.[6–10] The Re–Cl distances are significantly different and deserve some attention. The lengthening of the Re–Cl(2) bond [2.437(2) Å] *trans* to the multiply bonded oxygen atom can be reasonably ascribed to *trans* weakening, which is absent or negligible in the Re–Cl(1) bond [2.381(2) Å] *trans* to sulphur. The Re–P distance [2.488(2) Å] and the Re–N distance [2.087(5) Å] are normal if compared with other Re^V–P and Re^V–N distances in octahedral complexes.[6] The Re–S distance [2.406(2) Å] can be compared with values in the range 2.38—2.47 Å in two Re^V dithiocarbamates.[11] It is noteworthy that corresponding Re^I–S distances are significantly longer, ranging from 2.47 to 2.55 Å.

Bond distances in the chelate ligand show the C–S bond is single[12] while the double bond character is localized on the C–N bond [1.319(8) Å], and that, as a consequence, the negative charge of the bidentate anion should be mainly attributed to the sulphur atom. These and other structural details are fully comparable with those determined for the ligand $PhN{=}C(OEt)S^-$ in [$Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt)\}$].[1] Mean plane calculations show that the metal lies on the plane defined by S(1),N(1),Cl(1),P(1), the chelate moiety defined by S(1),N(1),C(19),O(2) being slightly inclined (by 8°) with respect to this plane. As in the above compound the attached phenylene ring is rotated about the N(1)–C(22) axis (by 50°).

Experimental

Solvents, when necessary, were purified and dried before use. The starting compounds [$ReOCl_3(PPh_3)_2$] and [$ReO(OR)Cl_2(PPh_3)_2$] (R = Me or Et) were prepared following the literature methods. The RNCS compounds were commercially available.[13] For the preparation of PhNC(OEt)SH and other technical details, see ref. 1.

Synthesis of the Complexes.—[$ReOCl_2(PPh_3)\{RN{=}C(OR')S\}$] [R = Ph, R′ = Et (**1**); R = p-MeC_6H_4, R′ = Et (**2**); R = Ph, R′ = Me (**3**); R = p-MeC_6H_4, R′ = Me (**4**)].—A large excess of the appropriate ligand RNCS (R = Ph or p-MeC_6H_4) was added to a benzene solution (40 cm³) of the compound [$ReO(OR)Cl_2(PPh_3)_2$] (0.18 mmol) (R = Et or Me). After 7—8 h at room temperature or 1—2 h at reflux temperature the green solution was filtered and then concentrated *in vacuo*. The resulting green precipitate was removed by filtration, and washed with EtOH and Et_2O. The complexes were crystallized from CH_2Cl_2–Et_2O.

Complex (**2**) was also obtained by the same procedure starting from [$ReOCl_3(PPh_3)_2$] or [$ReO(OEt)Cl_2(PPh_3)_2$] and using a large excess of the ligand PhNC(OEt)SH.

[$ReOCl_2(PPh_3)\{PhNC(OEt)S\}$] (**1**) (green): yield 80%, m.p. 175 °C (Found: C, 43.2; H, 3.4; N, 1.5; S, 4.0. Calc. for $C_{27}H_{25}Cl_2NO_2PReS$: C, 45.3; H, 3.5; N, 1.9; S, 4.5%). Infrared data (cm^{-1}, Nujol): ν(C$\overset{\cdots}{-}$N) 1 510; ν(Re≡O) 985; ν(Re–Cl) 315. ^{1}H N.m.r. ($CDCl_3$): δ 4.56 (q, CH_2); 1.47 (t, CH_3).

[$ReOCl_2(PPh_3)\{p\text{-}MeC_6H_4NC(OEt)S\}$] (**2**) (green): yield 70%, m.p. 173 °C (Found: C, 45.4; H, 3.7; N, 1.7; S, 3.7. Calc. for $C_{28}H_{27}Cl_2NO_2PReS$: C, 46.1; H, 3.7; N, 1.9; S, 4.4%). Infrared data (cm^{-1}, Nujol): ν(C$\overset{\cdots}{-}$N) 1 510; ν(Re≡O) 985; ν(Re–Cl) 310. ^{1}H N.m.r. ($CDCl_3$): δ 4.55 (q, CH_2); 2.35 (s, $CH_3C_6H_4$); 1.41 (t, CH_3CH_2).

Table 2. Final fractional atomic co-ordinates for (**2**)

Atom	*X/a*	*Y/b*	*Z/c*
Re(1)	0.333 40(2)	1.070 67(2)	0.313 87(3)
O(1)	0.362 29(35)	1.063 73(41)	0.482 88(45)
Cl(1)	0.236 24(13)	0.913 00(15)	0.279 31(20)
Cl(2)	0.264 30(14)	1.111 48(17)	0.075 14(16)
S(1)	0.461 71(13)	1.187 47(14)	0.285 61(18)
P(1)	0.173 28(12)	1.228 23(14)	0.341 97(16)
N(1)	0.469 40(39)	0.963 45(45)	0.253 46(54)
O(2)	0.618 98(35)	1.014 19(40)	0.204 37(50)
C(1)	0.053 24(42)	1.241 42(34)	0.212 95(54)
C(2)	−0.003 70(42)	1.354 53(34)	0.169 62(54)
C(3)	−0.096 87(42)	1.364 74(34)	0.073 36(54)
C(4)	−0.133 08(42)	1.261 84(34)	0.020 42(54)
C(5)	−0.076 13(42)	1.148 73(34)	0.063 74(54)
C(6)	0.017 03(42)	1.138 52(34)	0.160 01(54)
C(7)	0.202 39(41)	1.378 30(42)	0.353 95(45)
C(8)	0.258 13(41)	1.407 44(42)	0.258 18(45)
C(9)	0.283 80(41)	1.520 62(42)	0.262 83(45)
C(10)	0.253 72(41)	1.604 66(42)	0.363 26(45)
C(11)	0.197 98(41)	1.575 52(42)	0.459 03(45)
C(12)	0.172 32(41)	1.462 34(42)	0.454 38(45)
C(13)	0.130 23(30)	1.208 11(44)	0.501 33(44)
C(14)	0.194 34(30)	1.230 24(44)	0.623 61(44)
C(15)	0.163 08(30)	1.214 82(44)	0.746 38(44)
C(16)	0.067 70(30)	1.177 25(44)	0.746 88(44)
C(17)	0.003 59(30)	1.155 12(44)	0.624 60(44)
C(18)	0.034 85(30)	1.170 54(44)	0.501 82(44)
C(19)	0.526 62(48)	1.044 25(57)	0.243 36(63)
C(20)	0.681 21(58)	1.107 63(67)	0.197 19(80)
C(21)	0.747 50(66)	1 125 53(81)	0.333 46(94)
C(22)	0.503 15(37)	0.838 31(37)	0.230 88(36)
C(23)	0.498 15(37)	0.760 94(37)	0.331 04(36)
C(24)	0.533 65(37)	0.637 33(37)	0.314 63(36)
C(25)	0.574 17(37)	0.591 10(37)	0.198 07(36)
C(26)	0.579 18(37)	0.668 47(37)	0.097 91(36)
C(27)	0.543 67(37)	0.792 07(37)	0.114 32(36)
C(28)	0.613 78(90)	0.455 48(79)	0.183 08(130)
H(2)	0.024 33(42)	1.434 20(34)	0.210 61(54)
H(3)	−0.140 95(42)	1.452 31(34)	0.039 82(54)
H(4)	−0.205 20(42)	1.269 74(34)	−0.054 11(54)
H(5)	−0.104 17(42)	1.069 06(34)	0.022 76(54)
H(6)	0.061 12(42)	1.050 95(34)	0.193 55(54)
H(8)	0.281 42(41)	1.342 37(42)	0.180 43(45)
H(9)	0.326 95(41)	1.543 18(42)	0.188 68(45)
H(10)	0.273 59(41)	1.692 29(42)	0.366 87(45)
H(11)	0.174 70(41)	1.640 59(42)	0.536 79(45)
H(12)	0.129 17(41)	1.439 78(42)	0.528 53(45)
H(14)	0.268 18(30)	1.259 33(44)	0.623 23(44)
H(15)	0.212 71(30)	1.231 95(44)	0.841 05(44)
H(16)	0.043 50(30)	1.165 31(44)	0.841 93(44)
H(17)	−0.070 25(30)	1.126 03(44)	0.624 98(44)
H(18)	−0.014 78(30)	1.153 41(44)	0.407 16(44)
H(23)	0.466 78(37)	0.796 73(37)	0.421 28(36)
H(24)	0.529 78(37)	0.577 43(37)	0.392 17(36)
H(25)	0.601 66(37)	0.495 40(37)	0.185 36(36)
H(26)	0.610 54(37)	0.632 67(37)	0.007 67(36)
H(27)	0.547 55(37)	0.851 97(37)	0.036 78(36)

[ReOCl$_2$(PPh$_3$){PhNC(OMe)S}] (**3**) (green): yield 65%, m.p. 168 °C (Found: C, 43.6; H, 3.3; N, 1.9; S, 4.3. Calc. for $C_{26}H_{23}Cl_2NO_2PReS$: C, 44.6; H, 3.2; N, 2.0; S, 4.6%). Infrared data (cm^{-1}, Nujol): ν(C$\overset{\cdots}{-}$N) 1 510; ν(Re$\equiv$O) 985; ν(Re–Cl) 315. ^{1}H N.m.r. (CDCl$_3$): δ 4.56 (q, CH$_2$); 1.47 (t, CH$_3$).

[ReOCl$_2$(PPh$_3$){*p*-MeC$_6$H$_4$NC(OMe)S}] (**4**) (green): yield, m.p. 165 °C (Found: C, 43.3; H, 3.3; N, 1.4; S, 3.6. Calc. for $C_{27}H_{25}Cl_2NO_2PReS$: C, 45.3; H, 3.5; N, 1.9; S, 4.5%). Infrared data (cm^{-1}, Nujol): ν(C$\overset{\cdots}{-}$N) 1 520; ν(Re$\equiv$O) 985; ν(Re–Cl) 310. ^{1}H N.m.r. (CDCl$_3$): δ 4.02 (s, CH$_3$); 2.37 (s, C*H*$_3$C$_6$H$_4$).

X-*Ray Crystal Structure Determination of* [ReOCl$_2$(PPh$_3$)-{*p*-MeC$_6$H$_4$N=C(OEt)–S}] (**2**).—A well formed fragment of maximum dimension 0.2 mm was used for the *X*-ray work.

Crystal data. $C_{28}H_{27}Cl_2NO_2PReS$, $M = 729$, $a = 12.991(5)$, $b = 11.394(5)$, $c = 10.024(5)$ Å, $\alpha = 93.53(3)$, $\beta = 100.29(3)$, $\gamma = 77.74(3)°$, $U = 1\,426$ Å^3, $D_c = 1.70$ g cm^{-3} for $Z = 2$, μ(Mo-K_α) = 45 cm^{-1}, triclinic, space group $P\bar{1}$.

The intensities of 5 341 reflections were measured as described in ref. 1. Reference reflections recorded at regular intervals during data collection showed no significant change in intensity. The intensities were corrected for Lorentz polarization and absorption,[14] and 4 626 independent reflections with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations. The structure was solved by standard methods and refined to the final *R* factor of 0.035 when the maximum shift on the refined parameters was 0.1σ. Phenyl groups were refined as rigid bodies (C–C 1.395 Å, C–H 1.08 Å). For other procedural details regarding structure determination see ref. 1. Final atomic parameters are listed in Table 2, bond distances and angles in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

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