The Chemistry of Heteroallene and Heteroallyl Derivatives of Rhenium. Part 1. Reactivity of Mixed Carbonyl(formamido)(phosphine)rhenium(I) Complexes with RNCS (R = Ph or p-MeC$_6$H$_4$) and PhNCO. Crystal Structure of the Thiazetidine Rhenium(I) Complex [Re(CO)$_2$(PPh$_3$)$_2${PhN=C(OEt)–S}]†

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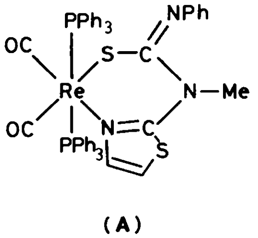
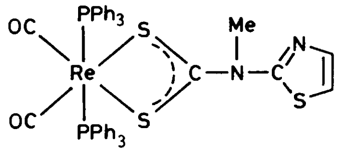
The formamido rhenium(I) compound [Re(CO)$_2$(PPh$_3$)$_2$(O$\cdots$CH$\cdots$NC$_6$H$_4$Me-p)] reacts in anhydrous benzene with an excess of PhNCS to give, after treatment with EtOH, the thioureido derivative [Re(CO)$_2$(PPh$_3$)$_2${PhN$\cdots$C[N(C$_6$H$_4$Me-p)CHO]$\cdots$S}] obtained by formal insertion of the heterocumulene molecule into the Re–N bond, and also the new thiazetidine rhenium(I) derivative [Re(CO)$_2$(PPh$_3$)$_2${PhN=C(OEt)–S}]. The crystal structure of the latter complex was determined by *X*-ray crystallography. The compound is monoclinic, space group $P2_1/n$, with a = 15.563(5), b = 19.156(4), c = 15.139(5) Å, β = 97.66(3)°, and Z = 4. The structure was refined to R = 0.054 for 5 886 independent reflections. The Re atom has distorted octahedral co-ordination. Selected bond distances are: Re–P 1.420 (mean), Re–S 2.548(4), Re–N 2.20(1), and Re–C 1.86 Å (mean).

Recently we have reported on the reactions of the aminothiazolato rhenium(I) complex [Re(CO)$_2$(PPh$_3$)$_2$(mat)] [mat = anion of 2-(methylamino)thiazole] and formamido rhenium(I) complex [Re(CO)$_2$(PPh$_3$)$_2$(O$\cdots$CH$\cdots$NC$_6$H$_4$Me-p)] with heterocumulenes such as RNCS (R = Ph or p-MeC$_6$H$_4$). These reactions under non-anhydrous conditions occur with displacement of the starting chelate ligands and formation of monothio- and dithio-carbamate complexes [Re(CO)$_2$(PPh$_3$)$_2${O–C(NHR)=S}] and [Re(CO)$_2$(PPh$_3$)$_2${S=C(NHR)–S}].[1] When the reaction with PhNCS and CS$_2$ is carried out on the complex [Re(CO)$_2$(PPh$_3$)$_2$(mat)] under anhydrous conditions, the thioureido, [Re(CO)$_2$(PPh$_3$)$_2${SC(NPh)NMe(C$_3$H$_2$NS)}], and dithiocarbamate, [Re(CO)$_2$(PPh$_3$)$_2${S$\cdots$C(mat)$\cdots$S}], rhenium(I) derivatives are obtained by formal insertion of heterocumulene molecules.[2] The first complex (**A**) arises from formal insertion of *e.g.* PhNCS into the Re–N(amino) bond of the starting chelate ligand giving rise to an expansion of the chelate four-membered ring to six-membered. In the second complex (**B**), the insertion of CS$_2$ gives rise to a four-membered ring.

The present paper reports the synthesis of the pseudoallyl (S,N; O,N) metal-bonded complexes [Re(CO)$_2$(PPh$_3$)$_2${X=C(OEt)–Y}] (X = PhN, Y = S; X = p-MeC$_6$H$_4$N, Y = S; X = PhN, Y = O).



(**A**)



(**B**)

Results and Discussion

[Re(CO)$_2$(PPh$_3$)$_2$(O$\cdots$CH$\cdots$NC$_6$H$_4$Me-p)] reacts with an excess of PhNCS in anhydrous PhH at reflux temperature to give the thioureido complex [Re(CO)$_2$(PPh$_3$)$_2${PhN$\cdots$C[N(C$_6$H$_4$Me-p)CHO]$\cdots$S}] (**1**) and the thiazetidine complex [Re(CO)$_2$(PPh$_3$)$_2${PhN=C(OEt)–S}] (**2**) by treating the concentrated reaction solution with EtOH. Complex (**1**) is obtained by formal insertion of the heterocumulene molecule into the Re–N bond.

When the reaction is carried out directly in the presence of the PhNC(OEt)SH ligand at room or at reflux temperature, only complex (**2**) is obtained. This complex can also be obtained from [Re(CO)$_3$(PPh$_3$)$_2$Cl] and the ligand in the deprotonated form.

The complex [Re(CO)$_2$(PPh$_3$)$_2${p-MeC$_6$H$_4$N=C(OEt)–S}] (**3**) was obtained by adding EtOH to the solution containing the formamido rhenium(I) complex and p-MeC$_6$H$_4$NCS at reflux temperature. The oxazetidine complex [Re(CO)$_2$(PPh$_3$)$_2${PhN=C(OEt)–O}] (**4**) is obtained by the same procedures by adding EtOH to a refluxing solution of the formamido complex and PhNCO, or by interaction between the salt of PhNHC(OEt)O with the tricarbonyl rhenium(I) complex. The reaction carried out using the urethane ligand and the formamido complex does not lead to substitution and the starting complex is recovered.

This last reaction probably proceeds *via* electrophilic attack of the acid proton of the ligand on the lone pair of the nitrogen atom co-ordinated to the metal. The different behaviour of the thiourethane and urethane ligands can be ascribed to the more acid character of the former, due to the 'mercaptide' character of the sulphur atom. Moreover, the urethane complex obtained by adding EtOH to a solution containing the formamido rhenium(I) complex and PhNCO under reflux suggests that the reaction can proceed *via* a reaction mechanism which does not involve the proton of the ligand.

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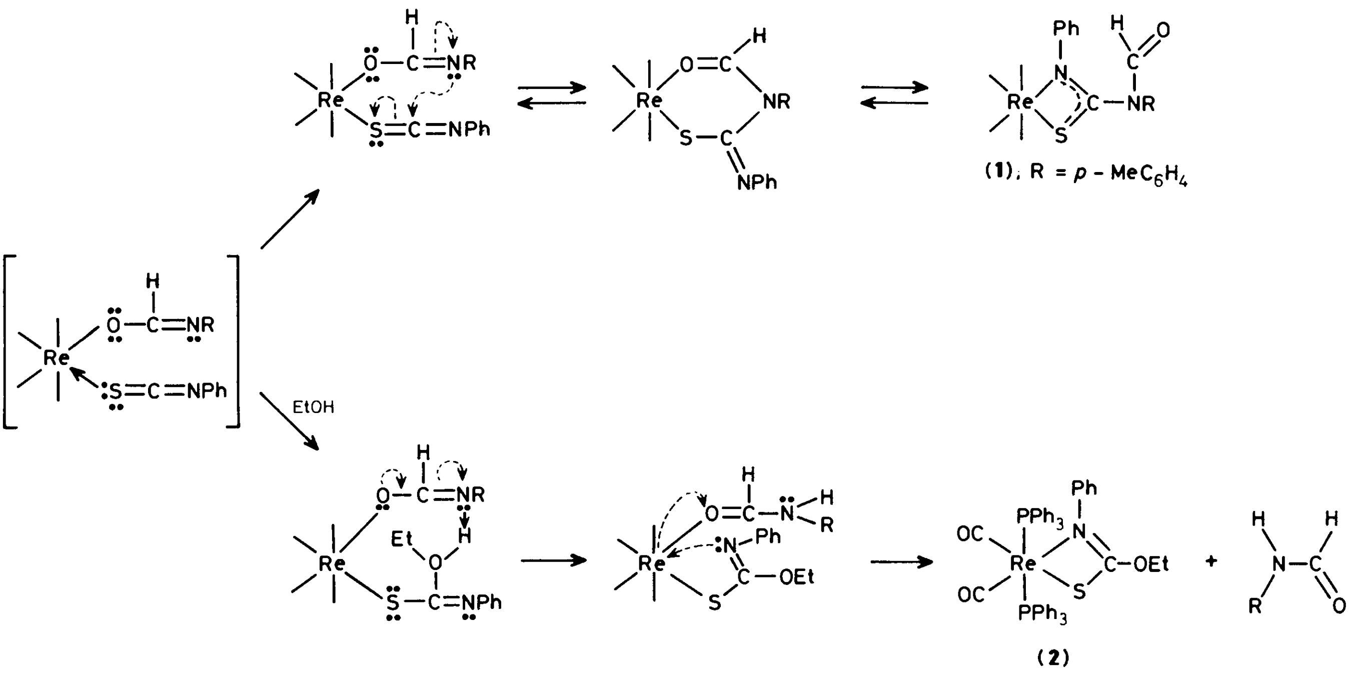
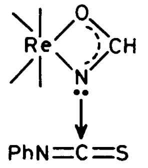
† Dicarbonyl[*O*-ethyl (phenylimino)thiocarbonato-*SN*]bis(triphenylphosphine)rhenium(I).

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

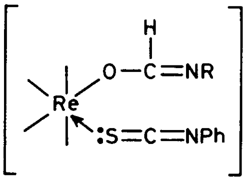


Scheme.

As far as the insertion reactions of heterocumulenes into M–N bonds are concerned, a possible mechanism involves an initial nucleophilic attack of a lone pair of the nitrogen atom on the electrophilic carbon of the heteroallene (see below).



However, the simultaneous formation of the thioureido and thiazetidine complexes using PhNCS and of the oxazetidine compound using PhNCO, suggests a mechanism providing the initial formation of an intermediate (**C**) in which the heterocumulene is σ-bonded to the metal atom (presumably using the sulphur atom in the case of PhNCS or the nitrogen atom in the case of PhNCO, considering the 'soft' character of the rhenium atom in a low oxidation state). This assumption can be explained taking into account the fluxional behaviour of the co-ordinated pseudoallyl ligand.[3] The intermediate complex may then evolve giving the insertion reaction or, in competition, it may react with an EtOH molecule forming the thioazetidine or oxazetidine derivatives as shown in the Scheme.



(**C**)

The complexes have been characterized by elemental analysis, i.r. and ^{1}H n.m.r. spectra (see Experimental section).

X-*Ray Structure of* [$Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt){-}S\}$] (**2**).—As shown in the Figure, the Re atom is six-co-ordinate distorted octahedral. The Re–P and Re–C distances are comparable with several determined previously, while the C–O bonds seem to be slightly longer than usually found in this type of compound.[4–8] The Re–S distance of 2.548(4) Å (Table 1) is relatively long compared with values in the range 2.47—2.51 Å found in other similar compounds,[2,8] whereas the Re–N distance of 2.20(1) Å compares well with corresponding values in Re$^{\text{I}}$ chelate complexes of triazenido, [RN$\cdots$N$\cdots$NR]$^-$, or amidino, [RN$\cdots$CR$\cdots$NR]$^-$ ligands.[5,6] The C–O(3)–C angle of 119° suggests that the oxygen atom can be considered to be in the sp^2 hybridized state, and the C–O bond lengths agree with the values expected for a C(sp^3)–O–C(sp^2) system.[9] The C–S bond distance of 1.72(1) Å is indicative of a C(sp^2)–S single bond,[10] whereas double bond character is well defined in the N–C(45) bond of 1.31(2) Å. Thus, the negative charge within the bidentate ligand seems to be mainly localized on the sulphur atom.

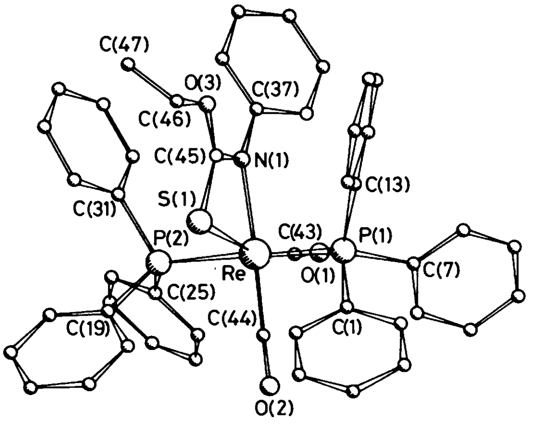


Figure. Crystal structure of [$Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt){-}S\}$] (**2**)

The Re atom lies exactly on the mean plane defined by the equatorial atoms S,N,C(43),C(44), which are essentially coplanar. The plane of the chelate moiety defined by S,N,C(45),O(3) is only slightly inclined (7.3°) to the equatorial

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

Re–P(1)	2.425(4)	Re–C(44)	1.87(1)	O(3)–C(46)	1.49(2)	P(2)–C(19)	1.845(8)
Re–P(2)	2.414(4)	N–C(45)	1.31(2)	C(46)–C(47)	1.40(3)	P(2)–C(25)	1.854(7)
Re–S	2.548(4)	N–C(37)	1.44(1)	P(1)–C(1)	1.845(8)	P(2)–C(31)	1.824(7)
Re–N	2.20(1)	S–C(45)	1.72(1)	P(1)–C(7)	1.844(7)	O(1)–C(43)	1.19(2)
Re–C(43)	1.86(1)	O(3)–C(45)	1.33(1)	P(1)–C(13)	1.840(6)	O(2)–C(44)	1.18(2)
P(1)–Re–P(2)	169.4(1)	Re–N–C(45)	101.9(8)	C(37)–N–C(45)	123.3(9)	C(7)–P(1)–C(13)	104.7(4)
S–Re–C(43)	163.3(4)	Re–C(43)–O(1)	178.0(1)	C(45)–O(3)–C(46)	119.0(1)	Re–P(2)–C(19)	114.8(3)
N–Re–C(44)	173.4(5)	Re–C(44)–O(2)	178.0(1)	O(3)–C(46)–C(47)	108.0(2)	Re–P(2)–C(25)	117.5(3)
S–Re–N	64.5(3)	Re–N–C(37)	134.8(7)	Re–P(1)–C(1)	114.7(3)	Re–P(2)–C(31)	115.0(3)
S–Re–C(44)	109.0(5)	S–C(45)–N	114.3(8)	Re–P(1)–C(7)	116.6(3)	C(19)–P(2)–C(25)	101.0(3)
N–Re–C(43)	98.8(5)	S–C(45)–O(3)	125.3(9)	Re–P(1)–C(13)	116.7(3)	C(19)–P(2)–C(31)	103.8(4)
C(43)–Re–C(44)	87.7(6)	N–C(45)–O(3)	120.0(1)	C(1)–P(1)–C(7)	99.9(4)	C(25)–P(2)–C(31)	102.7(4)
Re–S–C(45)	79.0(4)			C(1)–P(1)–C(13)	102.1(4)		

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

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	0.258 56(3)	0.218 73(3)	0.002 15(4)
S(1)	0.328 44(25)	0.117 90(19)	0.095 28(25)
P(1)	0.327 34(21)	0.169 40(18)	−0.118 27(22)
P(2)	0.187 99(22)	0.245 71(19)	0.130 65(23)
N(1)	0.385 74(68)	0.241 49(57)	0.079 10(69)
C(43)	0.236 09(83)	0.305 78(83)	−0.050 15(91)
C(44)	0.153 21(89)	0.188 71(79)	−0.059 48(97)
O(1)	0.224 17(77)	0.362 39(63)	−0.081 84(84)
O(2)	0.086 74(68)	0.171 43(71)	−0.099 95(77)
C(1)	0.282 00(50)	0.085 08(34)	−0.160 98(51)
C(2)	0.239 62(50)	0.041 47(34)	−0.106 94(51)
C(3)	0.207 27(50)	−0.022 86(34)	−0.139 27(51)
C(4)	0.217 30(50)	−0.043 59(34)	−0.225 64(51)
C(5)	0.259 69(50)	0.000 02(34)	−0.279 68(51)
C(6)	0.292 04(50)	0.064 35(34)	−0.247 35(51)
C(7)	0.317 27(42)	0.219 71(41)	−0.223 00(39)
C(8)	0.233 82(42)	0.241 04(41)	−0.257 53(39)
C(9)	0.219 17(42)	0.273 22(41)	−0.340 84(39)
C(10)	0.287 97(42)	0.284 06(41)	−0.389 62(39)
C(11)	0.371 43(42)	0.262 73(41)	−0.355 09(39)
C(12)	0.386 07(42)	0.230 56(41)	−0.271 78(39)
C(13)	0.443 70(33)	0.149 38(37)	−0.093 44(52)
C(14)	0.502 33(33)	0.204 68(37)	−0.080 25(52)
C(15)	0.590 78(33)	0.191 30(37)	−0.058 96(52)
C(16)	0.620 60(33)	0.122 62(37)	−0.050 86(52)
C(17)	0.561 97(33)	0.067 32(37)	−0.064 05(52)
C(18)	0.473 52(33)	0.080 70(37)	−0.085 34(52)
C(45)	0.407 52(72)	0.180 48(63)	0.114 78(79)
O(3)	0.486 17(64)	0.170 54(56)	0.159 26(68)
C(46)	0.508 31(129)	0.101 03(112)	0.200 48(141)
C(47)	0.536 24(167)	0.111 14(144)	0.291 46(181)
C(19)	0.123 79(46)	0.173 62(35)	0.169 39(50)
C(20)	0.108 44(46)	0.112 84(35)	0.119 00(50)
C(21)	0.057 24(46)	0.059 87(35)	0.147 71(50)
C(22)	0.021 38(46)	0.067 67(35)	0.226 82(50)
C(23)	0.036 74(46)	0.128 45(35)	0.277 21(50)
C(24)	0.087 94(46)	0.181 43(35)	0.248 50(50)
C(25)	0.106 96(39)	0.317 17(33)	0.119 47(44)
C(26)	0.059 00(39)	0.328 22(33)	0.036 03(44)
C(27)	−0.003 75(39)	0.380 62(33)	0.024 90(44)
C(28)	−0.018 54(39)	0.421 98(33)	0.097 20(44)
C(29)	0.029 41(39)	0.410 93(33)	0.180 64(44)
C(30)	0.092 16(39)	0.358 52(33)	0.191 77(44)
C(31)	0.260 75(45)	0.270 92(40)	0.230 06(44)
C(32)	0.284 74(45)	0.223 94(40)	0.299 37(44)
C(33)	0.341 44(45)	0.244 85(40)	0.373 88(44)
C(34)	0.374 15(45)	0.312 74(40)	0.379 07(44)
C(35)	0.350 15(45)	0.359 72(40)	0.309 76(44)
C(36)	0.293 45(45)	0.338 81(40)	0.235 26(44)
C(37)	0.440 28(40)	0.302 15(29)	0.092 05(44)
C(38)	0.495 51(40)	0.315 55(29)	0.170 60(44)
C(39)	0.545 80(40)	0.376 07(29)	0.178 40(44)
C(40)	0.540 87(40)	0.423 19(29)	0.107 65(44)
C(41)	0.485 64(40)	0.409 80(29)	0.029 10(44)
C(42)	0.435 35(40)	0.349 28(29)	0.021 31(44)

plane while the attached phenyl ring is somewhat rotated (35.1°) about the N–C(37) axis.

Experimental

Solvents, when necessary, were purified and dried before use. The syntheses were performed under dry argon. The starting compounds $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ and $[Re(CO)_3(PPh_3)_2Cl]$ were prepared following the literature methods;[7] RNCS (R = Ph or $p\text{-}MeC_6H_4$) and PhNCO were commercially available.

The ligands PhNC(OEt)SH and PhHNC(OEt)O were prepared by adding PhNCS to dried EtOH. The solution was evaporated to dryness and the residue was treated with n-hexane. The white product was recovered by filtration and then dried *in vacuo*. Other materials were reagent grade.

Infrared and ^1H n.m.r. spectra were recorded on Perkin-Elmer 577 and on WP 80-MHz Bruker spectrometers, respectively. Elemental analyses were performed on a Carlo Erba elemental analyser model 1106.

Synthesis of the Complexes.—$[Re(CO)_2(PPh_3)_2\{PhN\cdots C[N(C_6H_4Me\text{-}p)CHO]\cdots S\}]$ (**1**) *and* $[Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt){-}S\}]$ (**2**). (*a*). A large excess of PhNCS was added to a dry benzene solution (25 cm^3) of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4\text{-}Me\text{-}p)]$ (0.166 mmol). The mixture was heated at reflux temperature for 2 h and EtOH was added to the solution. The solid was filtered off, and washed with EtOH and Et_2O. The products were separated by thin-layer chromatography using silica-gel plates [2-mm thick; CH_2Cl_2–n-hexane (50:50) as eluant]. The complexes were crystallized from CH_2Cl_2–EtOH.

(*b*). Complex (**2**) was also obtained by stirring a benzene solution of the formamido rhenium(I) complex in the presence of an excess of PhNC(OEt)SH for 48 h at room temperature. Alternatively, complex (**2**) could be obtained by adding $[Re(CO)_3(PPh_3)_2Cl]$ to an anhydrous tetrahydrofuran (thf) solution of the salt of the ligand generated *in situ* by treating PhNC(OEt)SH with NaH. The mixture was refluxed for 1 h and then evaporated to one-third of its volume. The product was obtained upon addition of EtOH to this concentrated solution.

Complex (**1**) (yellow): yield 15%, m.p. 186 °C (Found: C, 60.5; H, 4.1; N, 2.6; S, 3.4. Calc. for $C_{53}H_{43}N_2O_3P_2ReS$: C, 61.4; H, 4.2; N, 2.7; S, 3.1%). Infrared data (cm^{-1}, Nujol): $\nu(C\equiv O)$ 1 930, 1 860; $\nu(C=O)$ 1 700; $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1 500. ^1H N.m.r. ($CDCl_3$): δ 7.05 (m, NC_6H_5); 6.60, 6.40 (m, C_6H_4); 2.30 (s, CH_3).

Complex (**2**) (white): yield 60%, m.p. 208 °C (Found: C, 58.4; H, 4.6; N, 1.3; S, 3.0. Calc. for $C_{47}H_{40}NO_3P_2ReS$: C, 59.6; H, 4.3; N, 1.5; S, 3.4%). Infrared data (cm^{-1}, Nujol): $\nu(C\equiv O)$ 1 915, 1 840; $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1 510; ν(C–O–C) 1 235. ^1H N.m.r. ($CDCl_3$): δ 6.77 (m, NC_6H_5); 3.47 (q, CH_2); 0.87 (t, CH_3).

$[Re(CO)_2(PPh_3)_2\{p\text{-}MeC_6H_4NC(OEt)S\}]$ (**3**). A large excess of *p*-MeC_6H_4NCS was added to a dry benzene solution (25 cm^3) of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ 0.166 mmol). The mixture was refluxed for 1 h and the solid product was obtained by adding EtOH to the concentrated solution. Complex (**3**) (white) was crystallized from CH_2Cl_2–EtOH: yield 60% (Found: C, 58.5; H, 4.3; N, 1.4; S, 3.1. Calc. for $C_{48}H_{42}NO_3P_2ReS$: C, 60.0; H, 4.4; N, 1.5; S, 3.3%). Infrared data (cm^{-1}, Nujol): $\nu(C\equiv O)$ 1 920, 1 850; $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1 510; ν(C–O–C) 1 240. ^1H N.m.r. ($CDCl_3$): δ 6.95 (m, NC_6H_4); 3.40 (q, CH_2); 2.17 (s, $CH_3C_6H_4$); 0.85 (t, CH_3CH_2).

$[Re(CO)_2(PPh_3)_2\{PhNC(OEt)O\}]$ (**4**). A large excess of PhNCO was added to a dry benzene solution (25 cm^3) of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4Me\text{-}p)]$ (0.166 mmol). The mixture was heated at reflux temperature for 2 h and then anhydrous EtOH (5.0 cm^3) was added and the reflux was maintained for another 20 min. The product was obtained by adding Et_2O to the solution concentrated to one-third of its volume. The volume was crystallized from thf–EtOH.

Complex (**4**) was also obtained by adding $[Re(CO)_3(PPh_3)_2Cl]$ to an anhydrous benzene solution of the salt of the ligand generated *in situ* by treating PhNHC(OEt)O with NaH and heating at reflux temperature for 1 h.

Complex (**4**) (white): yield 70%, m.p. 218 °C (Found: C, 59.9; H, 4.2; N, 1.3. Calc. for $C_{47}H_{40}NO_4P_2Re$: C, 60.1; H, 4.4; N, 1.5%). Infrared data (cm^{-1}, Nujol): $\nu(C\equiv O)$ 1 925, 1 840; $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1 510; ν(C–O–C) 1 270. ^1H N.m.r. ($CDCl_3$): δ 6.75 (m, C_6H_5N); 3.45 (q, CH_2); 0.76 (t, CH_3).

X-Ray Crystal Structure Determination of $[Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt){-}S\}]$ (**2**).—A well-formed fragment of maximum dimension 0.2 mm was used for the *X*-ray work.

Crystal data. $C_{47}H_{40}NO_3P_2ReS$, $M = 946$, $a = 15.563(5)$, $b = 19.156(4)$, $c = 15.139(5)$ Å, $\beta = 97.66(3)°$, $U = 4\,473$ Å^3, $D_c = 1.40$ g cm^{-3} for $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 30.2$ cm^{-1}, monoclinic, space group $P2_1/n$, general positions $\pm (x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$. The intensities of 7 908 reflections were measured up to $\theta = 25°$ on a Philips four-circle diffractometer with the $\theta/2\theta$ technique using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.7107$ Å). The compound remained stable under irradiation. The measured intensities were corrected for Lorentz polarization and for absorption,[11] and 5 886 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 conventional *R* factor of 0.054 when the maximum shift on the refined parameters was 0.2. Phenyl groups were refined as rigid bodies (C–C 1.395 Å). The quantity minimized in the refinement was $\Sigma w \Delta F^2$ with $w = 1$. Scattering factors for Re were from ref. 12, corrected for the anomalous dispersion; those for C, N, O, P, and S were supplied internally by the program SHELX.[13] 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.

Acknowledgements

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