The Coordination of N,N-Diethyl-N'-p-tolylthiourea to Polynuclear Rhenium Carbonyl Complexes

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The reactions of $Re_2(CO)_9(NCMe)$ and $Re_3(CO)_{10}$-$(CH_3CN)_2(\mu\text{-}H)_3$ with $S=C(NEt_2)N(H)(p\text{-tolyl})$ have yielded the new compounds $Re_2(CO)_9[S=C(NEt_2)N(H)(p\text{-tolyl})]$ (1) and $Re_3(CO)_{10}[\mu\text{-}SC(NEt_2)N(H)(p\text{-tolyl})](\mu\text{-}H)_3$ (2) in 89% and 98% yields, respectively. Compounds 1 and 2 were characterized by single-crystal X-ray diffraction analyses. Compound 1 contains an S-coordinated $S=C(NEt_2)N(H)(p\text{-tolyl})$ ligand terminally coordinated in an equatorial coordination site on one of the rhenium atoms. Compound 2 contains the first example of an S-coordinated bridging thiourea grouping. When solutions of 1 were heated to 97 °C, it was transformed to the new compound $\{Re(CO)_3[\mu\text{-}SC(N\text{-}p\text{-tolyl})(NEt_2)]\}_2$ (3) plus $Re_2(CO)_{10}$. Compound 3 is a centrosymmetrical dimer of the unit $Re(CO)_3[SC(N\text{-}p\text{-tolyl})(NEt_2)]$ in which the sulfur atom bridges the two rhenium atoms. The tolyl-substituted nitrogen atoms are coordinated to the rhenium atoms to form two Re−S−C−N rings.

In mononuclear metal complexes thioureas have been shown to be effective ligands through coordination of the sulfur atom[1]. However, in reactions involving polynuclear metal complexes the sulfur coordination is generally accompanied by a variety of bond rearrangements involving cleavage of C−S, C−N, N−H and/or C−H bonds in alkyl substituted derivatives[2−10]. For example, the addition of certain substituted thioureas to activated triosmium clusters has yielded edge and triply bridging thioureato ligands by coordination of the sulfur atom and cleavage of an N−H bond, e.g. Eq. (1)[3,8].
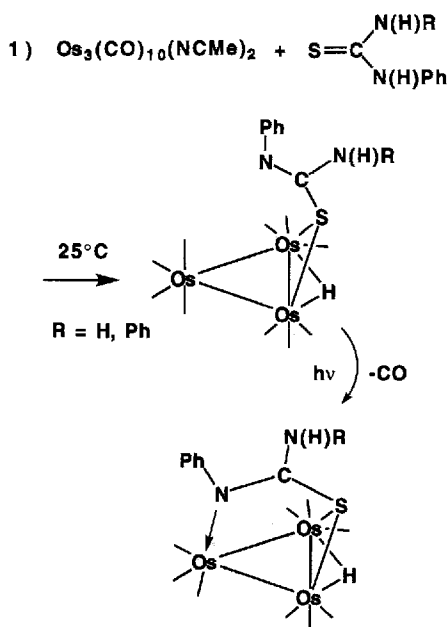
Under more forcing conditions cleavage of the C−S double bond occurs which leads to the formation of cluster complexes containing sulfido and diaminocarbene ligands, e.g. Eq. (2)[5].
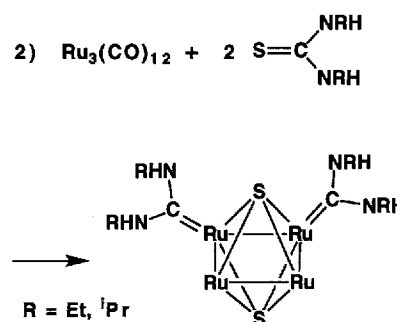
Interestingly, to date, there have been no reports on the coordination or reactions of thioureas with polynuclear rhenium carbonyl complexes.

As part of a continuation of our studies of the coordination of thioamido groups in rhenium complexes[11,12], we have investigated the reactions of $Re_2(CO)_9(NCMe)$ and $Re_3(CO)_{10}(CH_3CN)_2(\mu\text{-}H)_3$ with N,N-diethyl-N'-p-tolylthiourea, $Et_2NC=SN(H)(p\text{-tolyl})$. This has led to the synthesis of the substitution products, $Re_2(CO)_9[S=C(NEt_2)N(H)(p\text{-tolyl})]$ (1) and $Re_3(CO)_{10}[\mu\text{-}SC(NEt_2)N(H)(p\text{-tolyl})](\mu\text{-}H)_3$ (2). The latter compound contains the first example of a bridging thiourea ligand. When heated to 97 °C, compound 1 was transformed to the new compound $\{Re(CO)_3[\mu\text{-}SC(N\text{-}p\text{-tolyl})(NEt_2)]\}_2$ (3) and $Re_2(CO)_{10}$. Compounds 1−3 were characterized by single-crystal X-ray diffraction analyses. The results of these studies are reported herein.

Results

The reaction of $Re_2(CO)_9(NCMe)$ with N,N-diethyl-N'-p-tolylthiourea at 68 °C yielded the substitution product, $Re_2(CO)_9[S=C(NEt_2)N(H)(p\text{-tolyl})]$ (1) in 89% yield by replacement of the NCMe ligand with one quivalent of N,N-diethyl-N'-p-tolylthiourea. Compound 1 was characterized by IR, ^1H-NMR and a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of 1 is shown in Figure 1. The $Re_2(CO)_9$ portion of the molecule is structurally very similar to that of its parent $Re_2(CO)_9(NCMe)$ (4)[17], $Re_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (5)[18], $Re_2(CO)_9(\overline{SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2})$ (6)[19] and $Re_2(CO)_{10}$ (7)[20] with a staggered arrangement of the equatorial ligands on the two metal atoms. The Re−Re bond distance, 3.0466(7) Å, is similar to that in the related compounds 4, 3.039(1) Å, 5, 3.0422(8) Å, 6, 3.0554(8) Å and 7, 3.041(1) Å. The Re−S distance, 2.532(3) Å, is slightly longer than those to the thioether ligands in 5 and 6, 2.485(4) Å and 2.498(3) Å, respectively. The C−S double-bond distance, S−C(1) = 1.75(1), is slightly longer than those found for η^1-S-coordinated thiourea ligands in mononuclear complexes, 1.64(2)−1.72(1) Å[9], but is very similar to that observed for the η^1-S-coordinated tetramethylthiourea ligand in the complexes $Os_3(CO)_{11}[S=C(NMe_2)_2]$, 1.74(2) Å[21] and $Os_3(CO)_9(\mu\text{-OH})(\mu\text{-MeOC}=O)[S=C(NMe_2)_2]$, 1.739(13) Å[21]. The ^1H-NMR spectrum of 1 exhibits a broad singlet at $\delta = 7.42$ which is attributed to the hydrogen atom on the tolyl-substituted nitrogen atom. There is only one set of resonances 3.64 (q, br, $^3J_{H\text{-}H} = 7.0$ Hz, 4H, CH_2Me), 1.22 (t, $^3J_{H\text{-}H} = 7.0$ Hz, 6H, CH_3CH_2) for the two inequivalent ethyl groups of the NEt_2 grouping. This is attributed to an averaging process involving rotations of the NEt_2 grouping about the C−N(2) bond that are rapid on the NMR timescale.

The reaction of $Re_3(CO)_{10}(CH_3CN)_2(\mu\text{-H})_3$ with $S=C(NEt_2)N(H)(p\text{-tolyl})$ produced the new compound $Re_3(CO)_{10}[\mu\text{-SC}(NEt_2)N(H)(p\text{-tolyl})](\mu\text{-H})_3$ (2) in 98% yield. Compound 2 was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2. Compound 2 contains a triangular cluster of three rhenium atoms with one hydride ligand bridging each of the three rhenium−rhenium bonds. The cluster is very similar to that of other $Re_3(\mu\text{-H})_3$ clusters that have been structurally characterized[14,22]. The thiourea ligand is coordinated to an edge of the cluster through the sulfur atom. The Re−S distances, Re(1)−S(1) = 2.501(2) Å and Re(2)−S(1) = 2.489(2) Å, are slightly longer than the Re−S distances to the thiolato ligands in the complexes, $[PPN][Re_3(CO)_{10}(\mu\text{-SCH}_2CMe_2CH_2Cl)(\mu\text{-H})_3]$, 2.478(3) Å and $[PPN][Re_3(CO)_{10}(\mu\text{-SCH}_2CMe_2CH_2NMe_3)(\mu\text{-H})_3]$, 2.472(5) Å and 2.471(4) Å[14]. The C−S bond distance, 1.79(1) Å, is longer than that found in 1, 1.75(1) Å, where the sulfur is coordinated to only one metal atom. It is only slightly shorter than the C−S distance, 1.813(9) Å, found for the N,N-diphenylureato ligand in the complex $Os_3(CO)_{10}[\mu\text{-SC}(NHPh)(NPh)](\mu\text{-H})$[9] where the C−S bond order could be viewed formally as one. The reduction

Compound	1	2	3
formula	$Re_2SO_9N_2C_{21}H_{18}$	$Re_3O_{10}SN_2C_{22}H_{21}$	$Re_2S_2O_8N_4C_{30}H_{34}$
formula weight	846.86	1064.10	983.16
crystal system	triclinic	triclinic	triclinic
lattice parameters			
a (Å)	10.632(2)	13.570(4)	12.119(1)
b (Å)	14.283(2)	14.169(4)	9.818(1)
c (Å)	9.747(2)	9.171(2)	7.787(1)
α (°)	94.95(1)	90.54(2)	77.45(1)
β (°)	115.69(1)	107.75(2)	105.93(1)
γ (°)	86.31(1)	62.46(2)	87.84(1)
V (Å³)	1328.3(4)	1471(8)	864.9(2)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z value	2	2	1
$\rho_{calc.}$ (g/cm³)	2.12	2.40	1.89
μ (Mo $K\alpha$) (cm⁻¹)	92.4	124.4	71.6
temperature (°C)	20	20	20
$2\Theta_{max}$ (°)	48	44	50
no. obs. ($I>3\sigma$)	3222	3160	2793
no. variables	320	359	199
goodness of fit (GOF)*	2.07	1.57	1.48
residuals*: R, R_w	0.033; 0.035	0.024; 0.027	0.019; 0.023
abs. corr. (psi scans)	empirical	empirical	empirical
max. shift/error	0.02	0.00	0.00
largest peak in final diff. Fourier map (e⁻/Å³)	0.96	1.00	0.81

* $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}(|F_{obs}| - |F_{calc}|)/\sigma(F_{obs})]/(n_{data} - n_{vari})$.

Figure 1. An ORTEP diagram of the molecular structure of $Re_2(CO)_9[S=C(NEt_2)N(H)(p\text{-tolyl})]$ (1) showing 40%-probability thermal ellipsoids. Selected interatomic distances [Å] and angles [°]: Re(1)−Re(2) 3.0466(7), Re(2)−S 2.532(3), S−C(1) 1.75(1), C(1)−N(1) 1.34(1), C(1)−N(2) 1.30(1); Re(1)−Re(2)−S 84.89(6); Re(2)−S−C(1) 106.3(3), S−C(1)−N(1) 119.7(8), S−C(1)−N(2) 121.0(8)
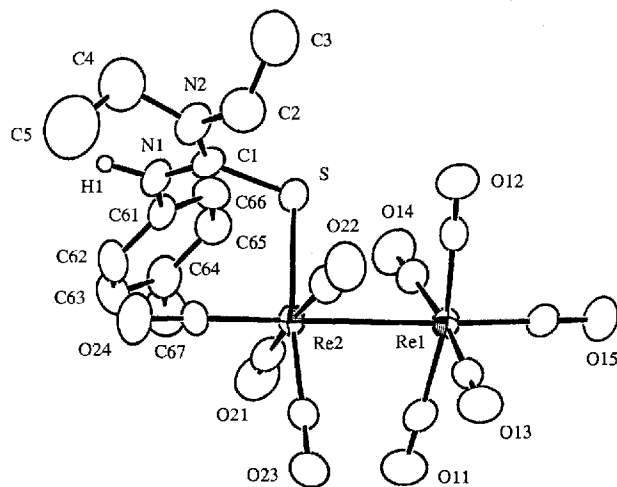
of the C−S bond order in 2 could be explained by a significant contribution of the polar resonance structure 2a.

Although the $S=C(NEt_2)N(H)(p\text{-tolyl})$ ligand is planar, the plane of the ligand is rotated 44.2° from the plane of the Re_3 cluster. The hydrogen atom H(4) on the nitrogen atom N(1) was located and refined in the structural analysis. It exhibits a characteristically deshielded resonance, $\delta = 8.30$, and is broad due to rapid relaxation caused by the quadrupolar effects on the neighboring nitrogen atom. The
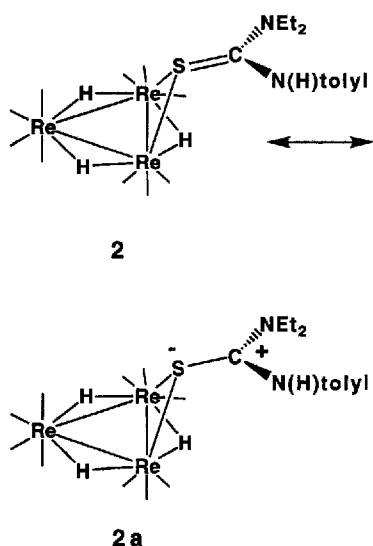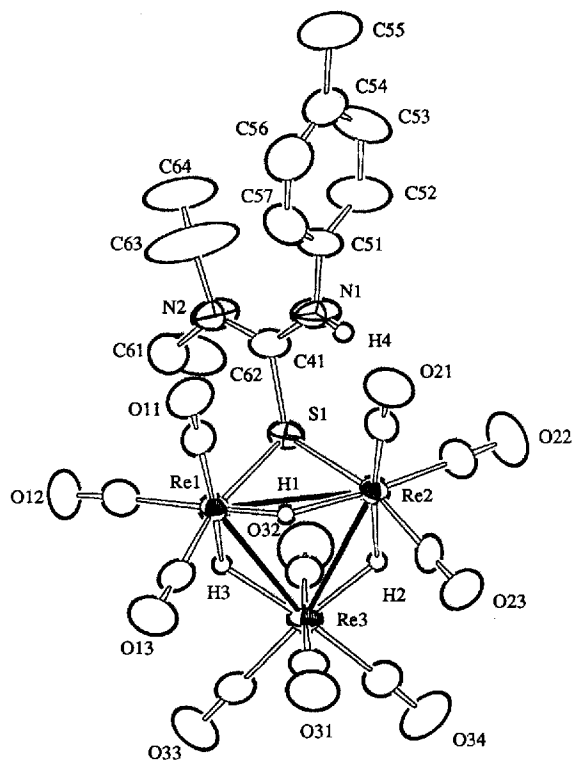
2

2 a

Figure 2. An ORTEP diagram of the molecular structure of $Re_3(CO)_{10}[\mu\text{-}SC(NEt_2)N(H)(p\text{-}tolyl)]$ (**2**) showing 50%-probability thermal ellipsoids. Selected interatomic distances [Å] and angles [°]: Re(1)−Re(2) 3.017(1), Re(1)−Re(3) 3.204(1), Re(2)−Re(3) 3.2243(8), Re(1)−S(1) 2.501(2), Re(2)−S(1) 2.489(2), S−C(41) 1.79(1), C(41)−N(1) 1.32(1), C(41)−N(2) 1.32(1); Re(3)−Re(1)−S(1) 75.83(6), Re(3)−Re(2)−S(1) 75.59(5), Re(1)−S(1)−Re(2) 74.40(6), S(1)−C(41)−N(1) 115.4(7), S(1)−C(41)−N(2) 117.8(7)


resonances of the ethyl groups are broad in the ¹H-NMR spectrum at room temperature presumably due to rotation about the C−NEt₂ bond as also observed in **1**. At −53 °C, these resonances are sharp indicating a slower rotation on the NMR timescale at this temperature. Interestingly, however the hydride resonances are observed as only two resonances in a 2:1 ratio at room temperature and at −53 °C.

According to the structural analysis all three hydride ligands are inequivalent. The observation of a two resonances suggests the existence of a rapid dynamical averaging process involving two of the three hydride ligands. A simple mechanism to average H(2) and H(3) could occur by a partial rotation of the C[NH(*p*-tolyl)](NEt₂) grouping about the C−S bond to generate a time averaged plane of symmetry perpendicular to the Re₃ plane.

When solutions of **1** in heptane solvent were heated to reflux (97 °C) for 4 h, the new compound {Re(CO)₃[μ-SC(N-*p*-tolyl)(NEt₂)]}₂ (**3**) was obtained in 84% yield. A significant amount of Re₂(CO)₁₀ was also formed in this reaction. Compound **3** was also obtained in very small amounts (≈1% yield) in the reaction of Re₂(CO)₉(NCMe) with *N,N*-diethyl-*N'*-*p*-tolylthiourea at 68 °C. Compound **3** was characterized by IR, ¹H-NMR and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3** is shown in Figure 3. The molecule lies on a crystallographic center of symmetry and is a dimer of the unit Re(CO)₃[SC(N-*p*-tolyl)(NEt₂)]. In the formation of **3** the substituted thiourea ligand in **1** was transformed into the thioureato ligand SC(*p*-tolylN)(NEt₂) by the loss of the hydrogen atom on the tolyl-substituted nitrogen atom. The sulfur atoms of the thioureato ligands in two fragments have come together to form bridges between two rhenium atoms producing a planar Re₂S₂ rhombus. Each thioureato ligand is a chelate formed by the coordination of the tolyl-substituted nitrogen atom to a rhenium atom. Chelating *N,N'*-diphenylthioureato ligands were structurally characterized in the complex Cr[SC(NPh)(NHPh)]₃ (**8**)[23]. The C−S distance of 1.793(4) Å in **3** is significantly longer than those in **8**, 1.733(3), 1.737(3) and 1.728(3) Å, where the sulfur atoms are terminally coordinated. This indicates that there is significantly less C−S multiple-bond character in **3** than in **8**. The rhenium atoms in **3** have 18-electron configurations without any direct bonding between the metal atoms. The Re⋯Re' distance of 3.8496(6) Å is consistent with this. The compound [Re(CO)₄[*E*-HC=C(CO₂Me)-CN(Ar)=S]Re(CO)₃]₂ (**9**) Ar = *p*-tolyl, has a similar dimeric structure with bridging thioamido groupings[12]. The Re⋯Re' and C−S distances in **9** are similar to those in **3**, 3.960(2) and 1.79(2) Å. The NEt₂ group in **3** is twisted 11.5° from the plane of the thioureato unit.

The resonances of the ethyl groups in **3** are broad at 25 °C due to an averaging process that can be explained by hindered rotation of the NEt₂ group about the C−N bond. However, at −53 °C all of the ethyl resonances are sharp and fully resolved: 3.68 (dq, 1H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 2.85 (dq, 1H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 2.63 (dq, 1H, $^2J_{H-H}$ = 14.0, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 2.46 (dq, 1H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 0.79 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH₂C*H₃*), 0.59 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH₂C*H₃*). The hydrogen atoms of the methylene groups are inequivalent. This results in the observation of four resonances as doublets of quartets. The methyl resonances average at high temperatures with coalescence at 42 °C, ΔG_{315^*} = 15.1 kcal/mol. At 90 °C the methyl resonances are averaged to a single sharp triplet at

Figure 3. An ORTEP diagram of the molecular structure of {Re(CO)₃[μ-SC(N-p-tolyl)(NEt₂)]}₂ (3) showing 50%-probability thermal ellipsoids. Selected interatomic distances [Å] and angles [°]: Re−N(1) 2.188(3), Re−S 2.513(1), Re−S' 2.555(1), C(1)−S 1.793(4), C(1)−N(1) 1.319(5), C(1)−N(2) 1.333(5), Re···Re' 3.8496(6); Re(1)−S−Re' 98.85(4), S−C(1)−N(1) 109.0(3)
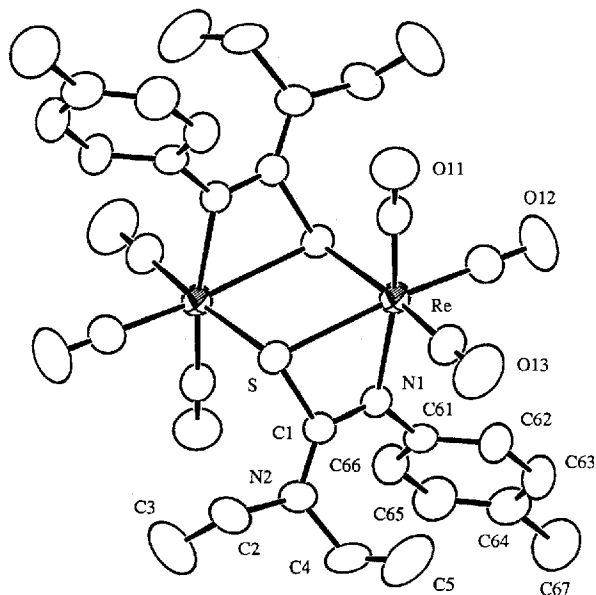

δ = 0.82. The four inequivalent hydrogen atoms on the two inequivalent methylene groups are averaged into two groups of two, 3.20 (s, br, 2H) and 3.01 (dq, 2H, ²J_{H-H} = 14.0 Hz, ³J_{H-H} = 7.0 Hz). This averaging can be explained by rotations about the C−NEt₂ bond.

Discussion

A summary of our investigation of the reactions of S=C(NEt₂)N(H)(p-tolyl) with Re₂(CO)₉(NCMe) is shown in Scheme 1. The formation of 1 occurs by a simple ligand-substitution reaction. The thermal decomposition of 1 involves the elimination of the hydrogen atom from the tolyl-substituted nitrogen atom and the Re(CO)₅ grouping leading to the formation of 3 and Re₂(CO)₁₀. The formation of Re₂(CO)₁₀ could occur via an intermediate formation of HRe(CO)₅, but at 97°C HRe(CO)₅ is known to be transformed to Re₂(CO)₁₀ and H₂[24]. Because the latter product is a gas, only the former product Re₂(CO)₁₀ was observed in this reaction. The monorhenium grouping Re(CO)₃[μ-SC(N-p-tolyl)(NEt₂)] is probably also formed in the initial transformation of 1, but even if the nitrogen atom is coordinated, this molecule would have only a 16-electron configuration. Accordingly, two of these units then condense to form the dimer 3 by employing a lone pair of electrons on the sulfur atoms to form bridging groups serving as three electron donors.

It has been shown that the addition of thioureas containing nitrogen-bound hydrogen atoms to triruthenium and triosmium clusters leads to the formation of N, S-coordinated edge and triply bridging ureato ligands by the transfer of an available hydrogen atom from one of the nitrogen atoms to the cluster, Eq. (1)[5,6,9,20]. In the complex Os₃(CO)₁₀[μ-SC(NHPh)(NPh)](μ-H) four electrons are do-

Scheme 1
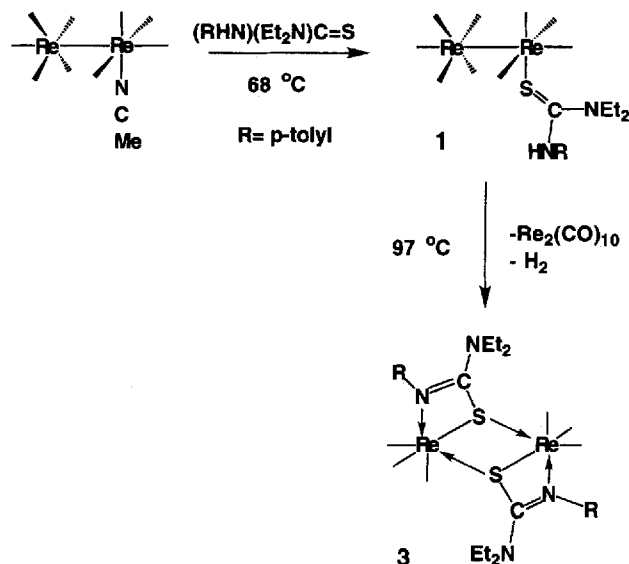
nated to the cluster by the combination of the ureato ligand (3 electrons) and the hydride ligand (1 electron). In contrast, the addition of S=C(NEt₂)N(H)(p-tolyl) to Re₃-(CO)₁₀(CH₃CN)₂(μ-H)₃ leads to the formation of 2 having sulfur coordination but without hydrogen transfer, Eq. (3).
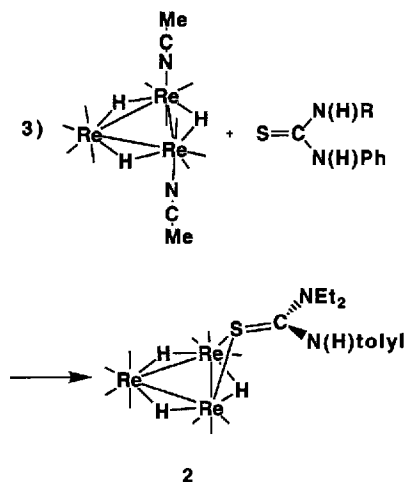
The thiourea ligand in 2 donates all four electrons to the cluster, all of which are derived from the sulfur atom. Transfer of the N-bound hydrogen atom to the cluster does not occur. This may be due to the fact that each metal−metal bond in the trirhenium cluster already contains a bridging hydride ligand and the addition of still another is unfavorable. Efforts to decarbonylate 2 thermally to produce selective activation of functional groupings on the thiourea ligand led only to degradation. A number of very low yield species seemed to form, but these could not be fully characterized.

Experimental

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Hexane and heptane solvents were freshly distilled from a sodium/benzophenone solution prior to use. – TLC separations were performed in air by using silica gel (60 Å, F_{254}) on glass plates (Whatman, 0.25 mm). – IR spectra: Nicolet 5DXB FT-IR spectrophotometer. – ^{1}H NMR: Bruker AM-400 spectrometer (400 MHz). Variable temperature ^{1}H-NMR spectra: Bruker AM-500 spectrometer (500 MHz, calibrated with methanol). – Elemental analyses: Desert Analytics, Tucson, AZ. – Mass spectra: VG Model 70SQ mass spectrometer (direct inlet, electron impact ionization). – $Re_2(CO)_9(MeCN)$[13] and Re_3-$(CO)_{10}(CH_3CN)_2(\mu$-H$)_3$[14] were prepared by previously published procedures. *N,N*-diethyl-*N'*-*p*-tolylthiourea was prepared by the reaction of Et_2NH with *p*-tolyl isothiocyanate by the established procedure[15].

Preparation of $Re_2(CO)_9[SC(NEt_2)N(H)(p$-tolyl$)]$ (**1**): A 100.0-mg amount (0.150 mmol) of $Re_2(CO)_9(MeCN)$, and a 40.0-mg amount (0.180 mmol) of *p*-tolylN(H)C=S(NEt$_2$) were dissolved in 50 ml of hexane. The solution was heated to reflux for 2 h. After cooling, the solvent was removed in vacuo, and the residue was separated by TLC using a hexane/CH$_2$Cl$_2$ (2:1) solvent mixture. This yielded in order of elution: 2.2 mg of $Re_2(CO)_{10}$; 2.0 mg of colorless {Re(CO)$_3$[μ-SC(N-*p*-tolyl)(NEt$_2$)]}$_2$ (**3**) 1% yield; 2.2 mg of unreacted $Re_2(CO)_9(MeCN)$ and 112.8 mg of pale yellow Re_2-$(CO)_9[SC(NEt_2)N(H)(p$-tolyl$)]$, **1**, 89% yield. – **1**: IR (hexane, cm^{-1}): $\tilde{v}_{CO}$ = 2101 (m), 2038 (s), 2011 (w), 1996 (vs), 1969 (s), 1965 (s), 1947 (w), 1919 (m), 1907 (m). – ^{1}H NMR (CDCl$_3$): δ = 7.42 (s, br, 1H, N*H*), 7.17 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, C$_6$*H*$_4$), 7.04 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, C$_6$*H*$_4$), 3.64 (q, br, $^3J_{H-H}$ = 7.0 Hz, 4H, MeC*H*$_2$), 2.33 (s, 3H, C*H*$_3$C$_6$H$_4$), 1.22 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, C*H*$_3$CH$_2$). – C$_{21}$H$_{18}$N$_2$O$_9$Re$_2$S (846.86): calcd. C 36.65, H 3.49, N 5.70; found C 36.49, H 3.30, N 5.60. – **3**: IR (hexane, cm^{-1}): $\tilde{v}_{CO}$ = 2015 (s), 1920 (s), 1908 (s). – ^{1}H NMR (CDCl$_3$, 25 °C): δ = 7.14 (s, 4H, C$_6$*H*$_4$), 3.77 (s, br, 1H, C*H*HMe), 3.24 (m, br, 2H, C*H*HMe), 3.10 (s, br, 1H, C*H*HMe), 2.34 (s, 3H, C*H*$_3$C$_6$H$_4$), 1.24 (s, br, C*H*$_3$CH$_2$), 0.95 (s, br, C*H*$_3$CH$_2$); ([D$_8$]toluene, –53 °C): δ = 7.47 (dd, 2H, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.2 Hz, C$_6$*H*$_4$), 7.35 (dd, 2H, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.2 Hz, C$_6$*H*$_4$), 3.68 (dq, 1H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 2.85 (dq, 1H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 2.63 (dq, 1H, $^2J_{H-H}$ = 14.0, $^3J_{H-H}$ = 7.0 Hz, CHHMe), 2.46 (dq, 1H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, CHHMe), 0.79 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH$_2$C*H*$_3$), 0.59 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, C*H*$_2$CH$_3$); ([D$_8$]toluene, 90 °C): δ = 7.26 (dd, 2H, $^3J_{H-H}$ = 8.0 Hz, C$_6$*H*$_4$), 6.97 (dd, 2H, $^3J_{H-H}$ = 8.0 Hz, C$_6$*H*$_4$), 3.2 (s, br, 2H, C*H*Me), 3.03 (dq, 2H, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 7.0 Hz, C*H*HMe), 0.82 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, CH$_2$C*H*$_3$). – MS: *m/z* = 984 (^{187}Re) and ions corresponding to the loss of each of the six carbonyl ligands. – C$_{30}$H$_{34}$N$_4$O$_6$Re$_2$S$_2$ (983.16): calcd. C 29.78, H 2.14, N 3.31; found C 29.77, H 1.97, N 3.27.

Synthesis of $Re_3(CO)_{10}[\mu$-SC(NEt$_2$)N(H)(p-tolyl$)](\mu$-H$)_3$ (**2**): A 50.0-mg of $Re_3(CO)_{10}(CH_3CN)_2(\mu$-H$)_3$ (0.054 mmol) and 12.0 mg (0.054 mmol) of S=C(NEt$_2$)N(H)(*p*-tolyl) was dissolved in 50 ml of CH$_2$Cl$_2$. The solution was stirred for 24 h at 25 °C. The solvent was then removed in vacuo and the colorless **2** was isolated from the residue by TLC using CH$_2$Cl$_2$/hexane (5:1) as elution solvent. Yield: 57.1 mg, 98%. – IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{v}_{CO}$ = 2102 (w), 2036 (m), 2017 (vs), 2004 (s), 1960 (m), 1928 (s). – ^{1}H NMR (CDCl$_3$, 25 °C): δ = 8.30 (s, br, 1H, N*H*), 7.23 (d, 2H, J_{H-H} = 8.3 Hz, C$_6$*H*$_4$), 6.99 (d, 2H, J_{H-H} = 8.3 Hz, C$_6$*H*$_4$), 4.15 (q, br, 2H, C*H*$_2$), 3.15 (q, br, 2H, C*H*$_2$), 2.36 (s, 3H, C*H*$_3$), 1.42 (t, br, 3H, C*H*$_3$), 1.01 (t, br, 3H, C*H*$_3$): –12.50 (s, 1H, Re$_2$*H*), –16.04 (s, 2H,

Re$_2$H); ([D$_8$]toluene, –53 °C): δ = 8.41 (s, br, 1H, N*H*), 6.49 (d, 2H, J_{H-H} = 8.3 Hz, C$_6$*H*$_4$), 6.39 (d, 2H, J_{H-H} = 8.3 Hz, C$_6$*H*$_4$), 3.52 (q, 2H, J_{H-H} = 7.1 Hz, C*H*$_2$), 2.14 (q, 2H, J_{H-H} = 7.1 Hz, C*H*$_2$), 1.87 (s, 3H, C*H*$_3$), 0.67 (t, 3H, J_{H-H} = 7.1 Hz, C*H*$_3$), 0.21 (t, 3H, J_{H-H} = 7.1 Hz, C*H*$_3$); –11.96 (s, 1H, Re$_2$*H*), –15.60 (s, 2H, Re$_2$*H*). – C$_{22}$H$_{21}$N$_2$O$_{10}$Re$_3$S (1064.10): calcd. C 24.81, H 1.97, N 2.63; found C 24.75, H 1.93, N 2.63.

Pyrolysis of **1**: A 20.0-mg amount (0.24 mmol) of **1** was dissolved in 20 ml of heptane. The solution was heated to reflux for 4 h. After cooling, a white precipitate was formed. The mother liquor was decanted and the precipitate was washed with 10 × 2-ml portions of hexane. The precipitate was recrystallized from a solution in hexane/CH$_2$Cl$_2$ (1:8) at room temperature to yield 9.4 mg of colorless crystals of {Re(CO)$_3$[μ-SC(N-*p*-tolyl)(NEt$_2$)]}$_2$ (**3**) in 81% yield. The mother liquor was concentrated and separated by TLC using hexane/CH$_2$Cl$_2$ (4:1). This yielded in order of elution: 4.0 mg of Re$_2$(CO)$_{10}$, 0.4 mg of **3**, and 2.1 mg of **1**. Combined yield of **3**: 9.8 mg, 84%.

Crystallographic Analyses: Crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained from solutions in hexane/CH$_2$Cl$_2$ (1:1) by slow evaporation of the solvent at 25 °C. Crystals of **3** were grown from a solution in hexane/CH$_2$Cl$_2$ (1:8) solvent mixture by slow evaporation of the solvent at 25 °C. The crystals used in diffraction analyses were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated MoK_α radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1[*]. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures[16a]. Empirical absorption corrections based on three azimuthal psi-scans were performed in each analysis. Anomalous dispersion corrections were applied to all non-hydrogen atoms[16b]. Full matrix least-squares refinements minimized the function:

$$\Sigma_{hkl}w(|F_o|-|F_c|)^2, \quad \text{where} \quad w = 1/\sigma(F)^2, \; \sigma(F) = \sigma(F_o^2)/2F_o$$

$$\text{and} \quad \sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp.$$

Compounds **1**–**3** all crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure in each case. All structures were solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL). All non-hydrogen atoms were obtained from difference Fourier syntheses, and all non-hydrogen atoms were refined with anisotropic thermal parameters.

In the analysis of **1** the hydrogen atom H(1) was located and refined with an isotropic thermal parameter. The positions of all other hydrogen atoms in **1** and all of those in **3** were calculated by assuming idealized geometries using observed positions whenever possible. For **2** the three hydride ligands were located and refined with an isotropic thermal parameter and the hydrogen atom H(4) on N(1) was located and refined on its positional parameters with a fixed thermal parameter, *B* = 6.0. All other hydrogen atom po-

[*] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59153.

sitions were calculated by assuming idealized geometries and were included in the structure factor calculations without refinement. The scattering contributions of all hydrogen atoms in calculated positions were added to the structure factor calculations but were not refined.

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