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Ligand exchange reactions starting from $[Re(CO)_3Br_3]^{2-}$. Synthesis, characterization and structures of rhenium(I) tricarbonyl complexes with thiourea and thiourea derivatives

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Abstract

The anionic rhenium(I) complex *fac*-$[Re(CO)_3Br_3]^{2-}$ has been reacted with thiourea (tu), *N,N*-dialkylbenzoylthioureas (HR_2btu) and *N,N*-dialkylthiocarbamoylbenzamidines ($HR^1{}_2tcbR^2$) to give novel mono- and binuclear rhenium(I) complexes. All new compounds are air-stable and non-sensitive against aqueous media. *Fac*-$[Re(CO)_3(tu)_3](NO_3)$ is formed from the bromo complex by precipitation of AgBr after addition of $AgNO_3$ and subsequent reaction with thiourea. The compound co-crystallizes with one molecule of $(Et_4N)NO_3$ in the monoclinic space group $P2_1/n$, $a=14.675(3)$, $b=13.372(1)$, $c=28.841(7)$ Å, $\beta=102.53(1)°$, $Z=8$. The mean Re–S bond length is 2.529 Å. *N,N*-Dialkylbenzoylthioureas react with $(Et_4N)_2[Re(CO)_3)Br_3]$ to form neutral $[Re(CO)_3Br(HR_2btu)]$ complexes. With the rhenium(I) centers under study they coordinate bidentately, but without deprotonation, which is unusual for this class of chelate ligands. $[Re(CO)_3Br(HEt_2btu)]$ crystallizes in the triclinic space group $P\bar{1}$, $a=8.080(2)$, $b=9.254(3)$, $c=13.761(5)$ Å, $\alpha=76.60(2)$, $\beta=88.66(2)$, $\gamma=70.92(3)°$, $Z=2$. The chelate ring shows significant deviations from planarity which underline the absence of an extended π-system. Complexes of different composition are formed with thiocarbamoylbenzamidines depending on the sterical requirements of the individual ligands. A binuclear compound could be isolated with *N,N*-diethylthiocarbamoylbenzamidinate (Et_2tcbH^-). $[Re_2(CO)_6(Et_2tcbH)_2]$ crystallizes in the monoclinic space group $P2_1/c$, $a=10.859(4)$, $b=17.409(2)$, $c=9.159(5)$ Å, $\beta=79.15(2)°$, $Z=2$. Both rhenium atoms are coordinated by three facially arranged carbonyls and a singly deprotonated Et_2tcbH^- ligand. The sulfur atoms of these ligands act as bridges between the metal centers forming a four-membered Re_2S_2 ring. Two slightly different Re–S bond lengths are observed in this ring system (2.507(2) and 2.545(2) Å). Only a mononuclear, anionic complex is formed with the more bulky benzamidine ligand *N*(*N*-morpholinylthiocarbonyl)-*N′*-phenylbenzamidine (Hmorphtcbph). $(Et_4N)[Re(CO)_3Br(morphtcbph)]$ crystallizes in the triclinic space group $P\bar{1}$, $a=10.018(4)$, $b=10.065(4)$, $c=16.720(7)$ Å, $\alpha=80.90(3)$, $\beta=79.82(3)$, $\gamma=70.81(4)°$, $Z=2$. The rhenium–sulfur distance is 2.476(2) Å.

Keywords: Rhenium complexes; Carbonyl complexes; Chelate complexes; Thiourea ligands; Crystal structures

1. Introduction

Rhenium compounds with the radioactive nuclide ^{186}Re are under discussion as radiopharmaceuticals in radioimmunotherapy [1,2]. The radiation characteristics of this β^--emitting isotope suggest a lower whole body radiation dose burden to the patient together with a high dose deposition at the tumor site than is observed with the frequently used ^{131}I. Chemical contributions to this field of nuclear medical research focus on the development of new procedures for the labeling of proteins with the metal.

As a consequence of the well-known radiopharmaceutical coordination chemistry of the chemically related element technetium, which is extensively used in diagnostic nuclear medicine, frequently high oxidation state complexes are used in protein labeling experiments. A new approach is the labeling of biomolecules with low-valent, organometallic rhenium compounds for radioimmunotherapy [3,4] and their technetium analogues for diagnostic purposes [4,5]. The application of carbonyl complexes became possible by the development of a low-pressure synthesis of $[M(CO)_3X_3]^{2-}$ anions (M = Re, Tc; X = Cl, Br) [3,4], which are convenient starting materials for ligand exchange reactions to obtain new technetium(I) and rhenium(I) compounds with the '*fac*-$M(CO)_3$' moiety. Autoclave reactions can be avoided by the

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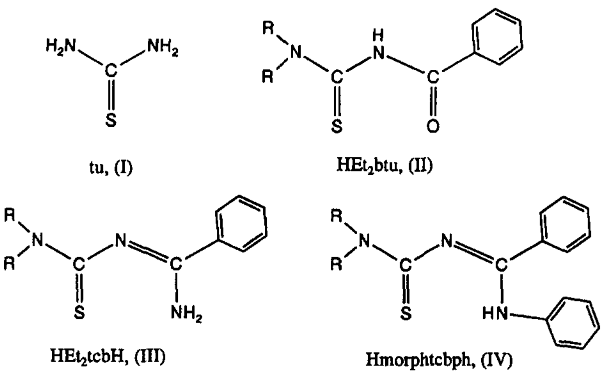

Scheme 1.

reduction of permetallates with BH_3 under a CO pressure of 1 atm. Thus, this method is very attractive for applications involving radioactive materials.

Numerous complexes with the facial $[Re(CO)_3]^+$ moiety are known from the literature [6]. However, $[Re(CO)_5Cl]$ was frequently used as the synthon for subsequent ligand substitutions which often results in the formation of a couple of products with low individual yields. The convenient high yield synthesis of $(Et_4N)_2[Re(CO)_3Br_3]$ recommends this compound as the preferable starting material for further syntheses. The three bromo ligands are labilized by the strong structural *trans* influence of the carbonyls and, thus, are expected to undergo ligand exchange with ligands of different size and donor atom sets.

In the present paper, we describe reactions of $(Et_4N)_2[Re(CO)_3Br_3]$ with thiourea (tu, **I**), *N,N*-diethylbenzoylthiourea (HEt_2btu, **II**), *N,N*-diethylthiocarbamoylbenzamidine (HEt_2tcbH, **III**) and *N*(*N*-morpholinylthiocarbonyl)-*N'*-phenyl-benzamidine (Hmorphtcbph, **IV**) (Scheme 1). All the ligands have a thiocarbonyl donor site which should be able to coordinate to metal ions. Depending on the metal centers, ligands **II**, **III** and **IV** are able to bind monodentately or as chelates [7,8].

2. Experimental

2.1. Syntheses

$(Et_4N)_2[Re(CO)_3Br_2]$ was prepared from tetrabutylammonium perrhenate, BH_3 and $(Et_4N)Br$ under an atmosphere of CO [4]. The chelate ligands were synthesized following literature procedures [9–12]. Thiourea was purchased commercially and used without further purification.

2.1.1. $[Re(CO)_3(tu)_3](NO_3)\cdot(Et_4N)NO_3$

89 mg (0.11 mmol) of $(Et_4N)_2[Re(CO)_3Br_3]$ were dissolved in 2 ml of water. Addition of 55 mg (0.33 mmol) of $AgNO_3$ gives an immediate precipitation. The AgBr was filtered off and 25 mg (0.33 mmol) of thiourea were added to the reaction solution. After 2 h stirring at room temperature the solvent was removed under vacuum. The remaining colorless oil was stirred with 5 ml of ether until a white powder was formed. This powder was dissolved in 1 ml of methanol and the solution was kept at −20 °C. After 2 days colorless crystals were formed and filtered from the solution. Yield 64 mg (77% based on Re).

Anal. Found: C, 22.5; H, 4.6; N, 16.6. Calc. for $C_{14}H_{32}N_9S_3O_9Re$: C, 22.3; H, 4.3; N, 16.7%. IR (cm^{-1}): ν(CO) 2020, 1918, 1888; ν(NH) 3316, 3180; ν(NO) 1384. FAB^+-MS: *m/z* 499 (M^+), 423 $[Re(CO)_3(tu)_2]^+$.

2.1.2. $[Re(CO)_3Br(HEt_2btu)]$

77 mg (0.1 mmol) $(Et_4N)_2[Re(CO)_3Br_3]$ were dissolved in 20 ml methanol and 120 mg (0.5 mmol) HEt_2btu were added. After addition of 2 drops Et_3N, the mixture was refluxed for 2 h and reduced in volume to about 5 ml. Upon standing overnight in a refrigerator, pale yellow crystals deposited which were removed by filtration. Yield 42 mg (72% based on Re).

Anal. Found: C, 31.1; H, 2.7; N, 4.4; S, 5.1%. Calc. for $C_{15}H_{16}BrN_2SO_4Re$: C, 30.7; H, 2.7; N, 4.8; S, 5.5%. IR (cm^{-1}): ν(CO) 2010, 1910. FAB^+-MS: *m/z* 586 (M^+), 530 $[Re(CO)Br(HEt_2btu)]^+$, 506 $[Re(CO)_3(Et_2btu)]^+$. ^{1}H NMR (ppm): NH 8.75 (s broad, 1H), phenyl 7.50–7.91 (m, 5H), CH_2 3.35 (m due to hindered rotation, 4H), CH_3 1.15 (m due to hindered rotation, 6H).

2.1.3. $[Re_2(CO)_6(Et_2tcbH)_2]$

77 mg (0.1 mmol) $(Et_4N)_2[Re(CO)_3Br_3]$ and 120 mg (0.5 mmol) HEt_2tcbH were dissolved in 50 ml methanol and 2 drops Et_3N were added. The mixture was refluxed for 2 h and reduced in volume until it became cloudy (about 10 ml). Upon cooling a light yellow precipitate was formed which was separated and recrystallized from CH_2Cl_2/MeOH. Yield 42 mg (84% based on Re).

Anal. Found: C, 35.7; H, 3.0; N, 8.7; S, 4.3. Calc. for $C_{30}H_{32}N_6S_2O_6Re_2$: C, 35.7; H, 3.2; N, 8.4; S, 6.3%. IR (cm^{-1}): ν(CO) 2008, 1920, 1884; ν(NH) 3365. FAB^+-MS: *m/z* 1010 (M^+), 982 $[Re_2(CO)_5(Et_2tcbH)_2]^+$, 926 $[Re_2(CO)_3(Et_2tcbH)_2]^+$, 868 $[Re_2(CO)(Et_2tcbH)_2]^+$, 840 $[Re_2(Et_2tcbH)_2]^+$. ^{1}H NMR (ppm): NH 7.74 s (1H), phenyl 7.40–7.98 (m, 5H), CH_2 3.88 (m due to hindered rotation, 4H), CH_3 1.32 (m due to hindered rotation, 6H).

2.1.4. $(Et_4N)[Re(CO)_3Br(morphtcbph)]$

77 mg (0.1 mmol) $(Et_4N)_2[Re(CO)_3Br_3]$ and 160 mg (0.5 mmol) Hmorphtcbph were dissolved in 20 ml methanol and 2 drops Et_3N were added. The mixture was refluxed for 2 h and reduced in volume to about 10 ml. Upon cooling a light yellow precipitate was formed which was separated and recrystallized from acetone/MeOH. A second crop of analytically pure product crystallized from the mother liquor upon standing overnight. Overall yield 52 mg (65% based on Re).

Anal. Found: C, 42.5; H, 4.5; N, 7.4; S, 4.6. Calc. for $C_{29}H_{38}N_4BrSO_4Re$: C, 43.2; H, 4.7; N, 7.0; S, 4.0%. IR (cm^{-1}): ν(CO) 1995, 1815; ν(NH) 3340. ^{1}H NMR (ppm):

phenyl 6.85–7.85 (m, 10H), morph 3.80+4.22 (m, 8H), CH_2I 4.01 (qu, 8H), CH_3 1.38 (tr, 12H).

2.2. *Physical measurements*

Routine IR spectra were recorded as KBr discs on a Specord 75 IR. Mass spectra were recorded on an MAT 701 A spectrometer (Finnigan). For the FAB^+ measurements xenon was used as primary beam gas. The ion gun was operated at 8 kV and 100 μA (probe temperature: 30 °C); nitrobenzylalcohol was used as matrix. The ^1H NMR spectra were recorded in acetone-d_6 and $CDCl_3$ solutions on a Bruker WM-400 with TMS as internal standard.

2.3. *X-ray diffraction*

The X-ray data were collected on an Enraf-Nonius CAD 4 diffractometer. The unit cell dimensions were determined from the angular settings of 25 high angle reflections. All structures were solved by the heavy-atom Patterson method (SHELXS-86 [13]). Refinement was performed with SHELXL-93 [14]. All non-hydrogen atoms were located from successive Fourier maps and refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and refined with the 'riding model' option of SHELXL-93 [14]. Absorption correction (psi scans and in the case of $[Re(CO)_3(tu)_3](NO_3)\cdot(Et_4N)NO_3$ DIFABS) was applied. The bromo ligand in $(Et_4N)[Re(CO)_3Br(morphtcbph)]$ was slightly disordered with the *trans* coordinated CO group (atoms C3 and O3). In the refinement an occupancy of 10% was considered for the Br atom at the opposite coordination site. The positions of the 10% occupancy of the corresponding C3′ and O3′ atoms could not be located from the Fourier maps and have not been included in the structure refinement. The final difference Fourier maps showed maximum peaks of 1.700 e Å^{-3} for $[Re(CO)_3(tu)_3](NO_3)\cdot(Et_4N)NO_3$, 2.485 e Å^{-3} for $[Re(CO)_3Br(HEt_2btu)]$, 0.461 e Å^{-3} for $[Re_2(CO)_6(Et_2tcbH)_2]$ and 1.537 e Å^{-3} for $(Et_4N)[Re(CO)_3Br(morphtcbph)]$ in the direct environment of the rhenium atoms. Crystal data and more details of the refinements are summarized in Table 1. See also Section 5. Positional parameters are given in Tables 2–5. The ORTEP drawings represent ellipsoids of 50% probability (in the case of the dimeric complex $[Re_2(CO)_6(Et_2tcbH)_2]$ 30% for clarity).

3. Results and discussion

$(Et_4N)_2[Re(CO)_3Br_3]$ can be prepared by a highly efficient low-pressure synthesis from perrhenate, $BH_3\cdot THF$ and $(Et_4N)Br$ under an atmosphere of CO (1 atm) [4] and, thus, is the preferable synthon for the preparation of new low-valent rhenium complexes having the '*fac*-$Re(CO)_3$' moiety. Ligand exchange reactions with the $[ReBr_3(CO)_3]^{2-}$ dianion can be performed under mild conditions which give access to a large number of organic ligands and normally provide high yields in analytically pure products. This is in contrast to most procedures starting from $[ReX(CO)_5]$ which require vigorous conditions and often result in poor product yields.

The bonding situation in $[Re(CO)_3Br_3]^{2-}$ is characterized by three labilized bromo ligands which can easily be substituted. This substitution normally takes place when the anion is dissolved in coordinating solvents such as acetonitrile, methanol or water. The course of this halide substitution, particularly in water, has been studied extensively by spectroscopic methods and potentiometric titrations [3]. The rate of the halide/solvent exchange can be increased by the addition of $Ag(BF_4)$ or $Ag(NO_3)$ depending on the solvent used. The resulting $[Re(CO)_3L_3]^{3+}$ species (L = solvent) easily react with the sulfur donor ligands summarized in Scheme 1.

The reaction with unsubstituted thiourea (tu) was carried out in water after addition of three aliquots $AgNO_3$ and precipitation of silver bromide. The resulting complex cation $[Re(CO)_3(tu)_3]^+$ can also be obtained without the removal of the bromide ions from the reaction mixture since the aqua complex $[Re(CO)_3(OH_2)]^+$ is immediately formed from $[Re(CO)_3Br_3]^{2-}$ after dissolving in water. This has been discussed in a previous paper [3] and can easily be checked by the positions of the carbonyl bands in the IR spectrum which are significantly shifted to higher wavenumbers upon addition of water. The obtained positions are identical with those of solutions from which all bromide was removed by the addition of silver ions [3]. However, we could only obtain crystalline products with a procedure which includes the precipitation of Br^- by silver nitrate and the filtration of the formed AgBr. This can easily be understood by the fact that the resulting $[Re(CO)_3(tu)_3](NO_3)$ co-crystallizes with one molecule of tetraethylammonium nitrate from the aqueous reaction mixture.

$[Re(CO)_3)(tu)_3](NO_3)$ is air-stable as a solid and in solution. The compound is readily soluble in water and alcohols, but only slightly soluble in non-polar organic solvents. The carbonyl part of the IR spectrum shows the typical pattern for a facial arrangement of the CO ligands and can be compared with the absorption in the previously reported $Re(CO)_3$ complexes with substituted thioureas ($[Re(CO)_3Cl(tu)_2]$ 2023, 1914 cm^{-1} [15] and $[Re(CO)_3(ethylentu)_3](ClO_4)$ 2022, 1912 cm^{-1} [16]). The FAB^+ mass spectrum is characterized by the molecular ion at $m/z = 499$. Fragmentation proceeds by the subsequent loss of complete ligands.

Colorless plates of X-ray quality could be obtained by the slow diffusion of ether into a solution of the reaction products in methanol. The compound crystallizes in the monoclinic space group $P2_1/n$ with two crystallographically independent $[Re(CO)_3(tu)_3](NO_3)$ and $(Et_4N)NO_3$ molecules per asymmetric unit. Anions and cations are well separated in the unit cell and no bonding contacts are evident. An ORTEP representation [17] of the complex cation is shown in Fig. 1. Selected bond distances and angles are summarized in Table 6. The rhenium atom is coordinated through a facial

Table 1
Crystal data collection and structure refinement parameters

	$[Re(CO)_3(tu)_3](NO_3) \cdot (Et_4N)(NO_3)$	$[Re(CO)_3Br(HEt_2btu)]$	$[Re_2(CO)_6(HEt_2tcb)_2]$	$(Et_4N)[ReBr(CO)_3(morphtcbph)]$
Crystal dimensions (mm)	0.4 × 0.25 × 0.15	0.15 × 0.15 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.05 × 0.05
Formula	$C_{14}H_{32}N_9O_9S_3Re$	$C_{15}H_{16}N_2O_4BrSRe$	$C_{30}H_{32}N_6O_6S_2Re_2$	$C_{29}H_{38}N_4O_4SBrRe$
Molecular weight	752.87	586.47	1009.14	804.80
Space group	monoclinic $P2_1/n$	triclinic $P\bar{1}$	monoclinic $P2_1/c$	triclinic $P\bar{1}$
Lattice dimensions				
a (Å)	14.675(3)	8.080(2)	10.859(4)	10.018(4)
b (Å)	13.372(1)	9.254(3)	17.409(2)	10.065(4)
c (Å)	28.841(7)	13.761(5)	9.159(5)	16.720(7)
α (°)	90	76.60(2)	90	80.90(3)
β (Å)	102.53(1)	88.66(2)	79.15(2)	79.82(3)
γ (Å)	90	70.92(3)	90	70.81(4)
V (Å^3)	5525(2)	944.4(5)	1701(1)	1557(1)
Z	8	2	2	2
D_c (g cm^{-3})	1.810	2.062	1.971	1.716
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Scan type	ω scan	ω scan	ω scan	ω scan
Absorption coefficient (cm^{-1})	46.84	86.79	72.85	52.89
Absorption correction	DIFABS	psi scans	psi scans	psi scans
T_{min}	0.853	0.843	0.783	0.9522
T_{max}	1.108	0.999	0.999	1.000
Range of h, k, l	$-1 \rightarrow 19, 0 \rightarrow 15, -39 \rightarrow 38$	$-1 \rightarrow 11, -12 \rightarrow 12, -18 \rightarrow 22$	$-1 \rightarrow 14, -24 \rightarrow 24, -12 \rightarrow 0$	$-1 \rightarrow 13, -13 \rightarrow 13, -22 \rightarrow 22$
Weighting scheme where $P = (F_o^2 + 2F_c^2)/3$	$1/\sigma^2(F_o^2) + 0.0270P)^2 + 15.6868P$	$1/\sigma^2(F_o^2) + (0.0764P)^2 + 2.3264P$	$1/\sigma^2(F_o^2) + (0.0225P)^2 + 1.5419P$	$1/\sigma^2(F_o^2) + (0.0087P)^2 + 5.2809P$
Total data (independent)	13980	5010	2670	8260
Observed data ($I > 2\sigma(I)$)	9832	4084	1911	5519
No. parameters	649	217	232	366
GOF	1.117	1.127	1.104	1.185
R_1	0.042	0.057	0.028	0.062
ωR_2	0.080	0.127	0.057	0.083
Measuring temperature (K)	208(2)	203(2)	293(2)	203(2)

Table 2
Atomic coordinates ($\times 10^4$) [a] for $[Re(CO)_3(tu)_3](NO_3)\cdot(Et_4N)(NO_3)$

Atom	x	y	z	U_{eq}
Re(1)	3739(1)	1553(1)	1019(1)	32(1)
S(1)	3044(1)	2791(1)	1505(1)	39(1)
S(2)	5054(1)	1738(1)	1746(1)	43(1)
S(3)	2892(1)	318(1)	1439(1)	36(1)
O(1)	2119(3)	1612(4)	152(2)	47(1)
O(2)	4817(4)	2975(4)	504(2)	68(2)
O(3)	4829(3)	−34(4)	601(2)	60(1)
N(1)	2013(4)	4419(4)	1389(2)	44(1)
N(2)	2482(4)	3914(4)	730(2)	43(1)
N(3)	6421(4)	653(5)	2224(2)	50(1)
N(4)	5109(4)	−228(4)	1913(2)	50(2)
N(5)	2060(4)	−1417(4)	1276(2)	50(2)
N(6)	2526(4)	−800(4)	637(2)	45(1)
C(1)	2734(4)	1569(5)	477(2)	36(1)
C(2)	4407(4)	2474(5)	711(2)	41(2)
C(3)	4403(4)	535(5)	756(2)	42(2)
C(4)	2478(4)	3766(5)	1179(2)	38(1)
C(5)	5554(4)	634(5)	1974(2)	38(1)
C(6)	2473(4)	−698(5)	1087(2)	34(1)
Re(11)	6275(1)	967(1)	3927(1)	32(1)
S(11)	7014(1)	−399(1)	3537(1)	42(1)
S(12)	5038(1)	673(1)	3179(1)	43(1)
S(13)	7131(1)	2089(1)	3452(1)	37(1)
O(11)	7871(4)	1081(4)	4808(2)	54(1)
O(12)	5040(4)	−325(4)	4414(2)	63(2)
O(13)	5161(4)	2668(4)	4259(2)	67(2)
N(11)	7509(4)	3295(5)	4206(2)	52(2)
N(12)	7505(4)	−1400(4)	4364(2)	44(1)
N(13)	4888(4)	2638(5)	3037(2)	59(2)
N(14)	7963(4)	3837(4)	3557(2)	49(2)
N(15)	7991(4)	−2033(4)	3732(2)	44(1)
N(16)	3605(4)	1716(5)	2732(2)	58(2)
C(11)	7560(4)	3144(5)	3767(2)	36(1)
C(12)	7533(4)	−1327(5)	3909(2)	36(1)
C(13)	4474(5)	1767(5)	2973(2)	44(2)
C(14)	5531(5)	120(6)	4233(2)	44(2)
C(15)	5597(5)	2041(5)	4134(2)	44(2)
C(16)	7258(4)	1039(5)	4480(2)	39(1)
N(20)	9834(3)	1409(4)	1191(2)	45(1)
C(21)	9577(5)	2192(6)	809(3)	50(2)
C(22)	10311(6)	2396(7)	528(3)	65(2)
C(23)	10638(5)	1759(6)	1579(3)	53(2)
C(24)	10482(7)	2711(8)	1830(3)	80(3)
C(25)	10145(6)	458(6)	993(3)	63(2)
C(26)	9437(8)	14(8)	580(4)	96(3)
C(27)	8976(5)	1238(7)	1396(3)	64(2)
C(28)	9068(6)	440(8)	1767(4)	86(3)
N(30)	4828(4)	6045(4)	1341(2)	46(1)
C(31)	4638(6)	5328(7)	921(3)	63(2)
C(32)	5429(7)	5236(7)	664(3)	77(3)
C(33)	5151(6)	7034(6)	1194(3)	66(2)
C(34)	4480(8)	7530(9)	787(4)	111(4)
C(35)	5606(5)	5644(6)	1731(3)	51(2)
C(36)	5438(7)	4631(7)	1924(3)	71(2)
C(37)	3930(5)	6138(8)	1512(4)	78(3)
C(38)	3957(7)	6883(9)	1905(4)	98(4)
N(40)	6807(3)	845(4)	471(2)	41(1)
O(41)	6776(3)	810(4)	900(2)	49(1)
O(42)	6753(5)	1640(4)	261(2)	73(2)
O(43)	6905(4)	49(4)	258(2)	57(1)
N(50)	1802(4)	6483(4)	449(2)	42(1)
O(51)	1781(4)	7298(4)	246(2)	63(2)
O(52)	1763(3)	6441(4)	877(2)	50(1)
O(53)	1848(4)	5700(4)	223(2)	64(2)
N(60)	1940(4)	9474(5)	2408(2)	48(2)
O(61)	2191(7)	10200(7)	2640(2)	136(4)
O(62)	1185(5)	9430(6)	2155(3)	99(2)
O(63)	2449(6)	8777(8)	2415(3)	137(4)
N(70)	8144(4)	2891(6)	2469(2)	51(2)
O(71)	8955(4)	2960(5)	2687(2)	77(2)
O(72)	7613(5)	3583(7)	2504(2)	99(3)
O(73)	7884(6)	2163(6)	2235(2)	109(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter U_{eq} which is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) [a] for $[Re(CO)_3Br(HEt_2btu)]$

Atom	x	y	z	U_{eq}
Re	857(1)	3593(1)	2403(1)	25(1)
Br	−1146(1)	2568(1)	1457(1)	41(1)
S	2505(3)	807(2)	3159(2)	27(1)
O1	−1535(15)	3794(13)	4153(9)	84(4)
O2	−1098(13)	7017(9)	1333(8)	66(3)
O3	3184(16)	4654(11)	3488(6)	63(3)
O4	2564(10)	3139(9)	1214(6)	41(2)
C1	−641(15)	3762(12)	3476(9)	44(3)
C2	−360(14)	5740(11)	1711(8)	38(2)
C3	2395(16)	4304(11)	3104(8)	39(2)
N1	5168(9)	1424(9)	2128(6)	28(2)
N2	5890(10)	−634(9)	3516(6)	29(2)
C4	4657(11)	534(9)	2918(7)	25(2)
C5	4193(11)	2320(9)	1226(6)	23(2)
C6	5451(12)	−1637(10)	4403(7)	29(2)
C7	4963(17)	−2958(12)	4172(9)	47(3)
C8	7794(13)	−1113(13)	3305(9)	47(3)
C9	8761(16)	−419(19)	3890(10)	69(5)
C11	5168(12)	2207(10)	313(7)	26(2)
C12	4734(14)	3480(11)	−510(7)	36(2)
C13	5563(16)	3414(15)	−1378(9)	48(3)
C14	6935(18)	2061(16)	−1431(9)	53(3)
C15	7377(14)	760(14)	−616(9)	44(3)
C16	6501(13)	849(11)	258(8)	33(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter U_{eq} which is defined as one third of the trace of the orthogonalized U_{ij} tensor.

arrangement of three carbonyl and three thiourea ligands in a slightly distorted octahedral arrangement. The Re–C bond lengths are in the range between 1.902(6) and 1.922(7) Å. The mean value for the Re–S distance in the $[Re(CO)_3(tu)_3]^+$ cation is 2.529 Å.

Dialkylbenzoylthioureas (**II**) are excellent ligands and form chelate complexes with a large number of metals [7]. This usually goes along with deprotonation and the formation of an extended π-system in the six-membered chelate rings. In acidic media, however, the deprotonation can be suppressed and benzoylthioureas coordinate monodentately

Table 4
Atomic coordinates ($\times 10^4$) [a] for $[Re_2(CO)_6(HEt_2tcb)_2]$

Atom	x	y	z	U_{eq}
Re	3952(1)	295(1)	1846(1)	38(1)
S	4250(2)	617(1)	−866(2)	41(1)
O1	1609(7)	1278(3)	2665(10)	90(4)
O2	3675(8)	−250(3)	5069(7)	71(3)
O3	5404(7)	1685(3)	2692(7)	67(3)
N1	2227(7)	−351(3)	−933(8)	49(3)
N2	3001(7)	−701(3)	1207(8)	38(3)
N3	2134(9)	855(4)	−1848(11)	61(4)
C1	2489(9)	898(4)	2371(10)	57(4)
C2	3766(9)	−43(4)	3844(9)	48(3)
C3	4894(8)	1156(4)	2342(9)	43(3)
C4	2764(8)	336(4)	−1219(9)	42(3)
C5	2512(7)	−853(3)	55(9)	36(3)
C6	765(10)	674(5)	−2018(12)	61(5)
C7	801(12)	253(5)	−3355(10)	85(6)
C8	2579(11)	1677(5)	−2222(12)	87(5)
C9	3207(17)	1737(7)	−3738(16)	164(11)
C11	2079(8)	−1665(4)	−175(9)	40(3)
C12	2644(10)	−2283(4)	369(11)	48(4)
C13	2221(13)	−3021(5)	200(13)	63(5)
C14	1248(15)	−3140(6)	−461(13)	76(7)
C15	670(12)	−2534(8)	−1010(18)	72(6)
C16	1102(11)	−1789(5)	−864(11)	56(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter U_{eq} which is defined as one third of the trace of the orthogonalized U_{ij} tensor.

via sulfur [7,18]. The reaction of diethylbenzoylthiourea (HEt_2btu) with $(Et_4N)_2[Re(CO)_3)Br_3]$ gives pale yellow crystals of $[Re(CO)_3Br(HEt_2btu)]$ which can easily be separated from the reaction mixture.

The neutral complex is soluble in CH_2Cl_2 or chloroform. No decomposition could be detected in solution over a period of 4 weeks. As expected, facial coordination of the CO ligands could be derived from the IR spectrum of the complex. An IR band for the NH vibration of the benzoylthiourea could not be assigned unambiguously. A broad signal at 8.75 ppm in the proton NMR spectrum of the diamagnetic complex, however, suggests that the ligand coordinates without deprotonation.

Crystals suitable for X-ray diffraction could be obtained from the slow evaporation of a $CHCl_3$/MeOH solution. The complex crystallizes triclinic in the space group $P\bar{1}$. The structure consists of well separated neutral complex molecules. An ORTEP plot together with the atomic numbering scheme is given in Fig. 2. Typical bond lengths and angles are contained in Table 7. The rhenium atom in $[Re(CO)_3Br(HEt_2btu)]$ is coordinated in a nearly ideal octahedral geometry. Besides three facially positioned carbonyl ligands the metal coordinates one molecule of diethylbenzoylthiourea and one bromo ligand. Diethylbenzoylthiourea acts as a bidentate ligand with oxygen/sulfur donor sites. In contrast to the situation in other metal chelates with this ligand [7], it is not deprotonated in $[Re(CO)_3Br(HEt_2btu)]$. This is clearly indicated by the formation of a neutral complex which contains one bromo ligand at the 'fac-$Re(CO)_3{}^+$' core. Further evidence of this bonding mode is given by the non-planarity of the six-membered chelate ring in $[Re(CO)_3Br(HEt_2btu)]$. For the deprotonated ligand an extended π-system is expected with an almost planar chelate ring. The wire model in Fig. 2 illustrates the significant deviations from planarity in the rhenium(I) carbonyl compound. The Re–O4 bond length of 2.142(8) Å is in the same range as those in hydroxo bridged tricarbonylrhenium(I) clusters [3] and $[Re(CO)_3Br(pic)]^-$ (Hpic = picolinic acid) [19]. However, the O4–C5 bond distance in $[Re(CO)_3Br(HEt_2btu)]$ is somewhat shorter than in the planar palladium

Table 5
Atomic coordinates ($\times 10^4$) [a] for $(Et_4N)[ReBr(CO)_3(morphtcbph)]$

Atom	x	y	z	U_{eq}
Re	1672(1)	1039(1)	2320(1)	27(1)
Br	2334(1)	−969(1)	1337(1)	35(1)
S	3833(2)	1580(2)	1580(1)	33(1)
O1	−182(7)	3064(6)	1084(4)	42(2)
O2	−989(7)	297(7)	3213(4)	45(2)
O3	1039(12)	3414(10)	3386(7)	68(4)
O4	6294(8)	5008(7)	2229(5)	64(2)
N1	3117(7)	−408(6)	3161(4)	28(2)
N2	4853(7)	749(7)	3042(4)	31(2)
N3	5000(8)	2860(7)	2410(4)	37(2)
N4	8409(7)	7911(6)	1317(4)	26(2)
C1	502(9)	2295(9)	1551(5)	31(2)
C2	18(9)	558(8)	2889(5)	31(2)
C3	1288(11)	2558(13)	2999(6)	41(3)
C4	4332(8)	−344(8)	3304(5)	26(2)
C5	4568(8)	1712(8)	2414(5)	29(2)
C6	5684(10)	3042(10)	3066(6)	48(3)
C7	6819(11)	3694(9)	2708(6)	49(3)
C8	5713(14)	4785(12)	1566(7)	76(4)
C9	4533(10)	4184(10)	1856(7)	55(3)
C11	5264(8)	−1451(8)	3865(5)	28(2)
C12	6054(9)	−1037(9)	4322(5)	39(2)
C13	6867(10)	−2005(10)	4866(6)	48(3)
C14	6917(10)	−3386(10)	4956(5)	45(3)
C15	6181(10)	−3833(9)	4491(6)	45(2)
C16	5355(9)	−2875(9)	3944(6)	38(2)
C21	2439(9)	−1357(8)	3693(5)	31(2)
C22	2182(10)	−2455(9)	3394(5)	41(2)
C23	1221(10)	−1978(10)	5001(6)	50(3)
C24	965(9)	−3041(10)	4681(7)	50(3)
C25	1466(10)	−3260(9)	3861(6)	38(2)
C26	1949(10)	−1147(9)	4505(5)	40(2)
C31	6843(8)	8095(8)	1342(5)	30(2)
C32	6354(9)	8219(10)	519(5)	42(2)
C33	8821(8)	9100(8)	760(5)	31(2)
C34	7943(10)	10578(8)	990(6)	42(2)
C35	8702(8)	7924(8)	2170(4)	30(2)
C36	8640(10)	6644(10)	2748(5)	47(2)
C37	9277(8)	6511(8)	976(5)	33(2)
C38	10855(9)	6104(9)	985(6)	48(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter U_{eq} which is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The Br atom is disordered at the position 0.1230(16), 0.3041(16), 3201(10) by an occupancy of 10%. The positions of the corresponding CO group have not been regarded in the refinement.

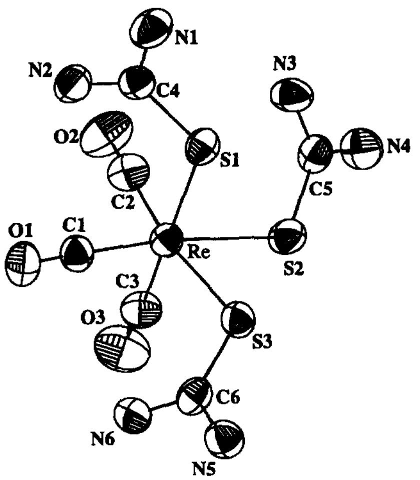

Fig. 1. ORTEP plot [17] of the complex cation in $[Re(CO)_3(tu)_3](NO_3)$. Hydrogen atoms are omitted for clarity.

chelate with the same ligand [20]. This reflects the lower extent of electron delocalization from the C–O double bond in the present rhenium(I) carbonyl compound.

N,N-Dialkylthiocarbamoylbenzamidines (**III** and **IV**) are known to have coordination properties which are very similar to those of benzoylthioureas. They form chelate complexes as singly deprotonated N,S-donor ligands with a number of metals [8]. This coordination is characterized by an almost planar six-membered chelate ring and has also been realized for oxo and nitrido complexes of rhenium(V) [21–23]. The reaction with $[Re(CO)_3Br_3]^{2-}$ gives complexes of different composition depending on the sterical requirements of the ligands. With ligand **III** a dimeric complex is formed where the *N,N*-dialkylthiocarbamoylbenzamidinate acts as a bridging ligand via its sulfur atom. Compounds of this general type have previously been described as products of reactions between rhenium carbonyls and a chelating ligand with sulfur donors [6]. For *N,N*-dialkylthiocarbamoylbenzamidinates, however, the bridging coordination between two metal centers is unusual. The more bulky ligand **IV** is obviously unable to realize the same coordination. Thus, only an anionic complex with one remaining bromo ligand is formed. In both new compounds the chelating ligands are deprotonated.

$[Re_2(CO)_6(Et_2tcbH)_2]$ can be obtained in the form of yellow plates which are readily soluble in organic solvents like chloroform or benzene and only slightly soluble in alcohols. The ligand is singly deprotonated. The IR band of the remaining NH vibration can be detected as a sharp absorption at 3365 cm^{-1}. The carbonyl range of the spectrum gives evidence for the facial coordination of the CO ligands. FAB^+ mass spectra show the molecular ion of the binuclear compound with only low intensity (about 3% B). Starting from this low intensity peak fragmentation can be detected which is characterized by the stepwise loss of carbonyl ligands.

Crystals of $[Re_2(CO)_6(Et_2tcbH)_2]$ suitable for a crystallographic study could be obtained from CH_2Cl_2/iso-propanol solutions. The compound crystallizes monoclinic with two dimeric units per unit cell. The dimeric units are generated

Table 6
Selected bond lengths and angles in both independent complex cations of $[Re(CO)_3(tu)_3](NO_3)\cdot(Et_4N)NO_3$ with e.s.d.s

Bond lengths (Å)					
Re1–C1	1.902(6)	Re1–C2	1.909(6)	Re1–C3	1.922(7)
Re1–S1	2.552(2)	Re1–S2	2.529(2)	Re1–S3	2.536(2)
C1–O1	1.152(7)	C2–O2	1.149(7)	C3–O3	1.137(8)
S1–C4	1.713(7)	S2–C5	1.714(7)	S3–C6	1.727(6)
Re11–C11	1.905(6)	Re11–C12	1.917(7)	Re11–C13	1.916(7)
Re11–S11	2.512(2)	Re11–S12	2.531(2)	Re11–S13	2.541(2)
C11–O11	1.159(7)	C12–O12	1.143(8)	C13–O13	1.158(8)
S11–C14	1.707(7)	S12–C15	1.722(7)	S13–C16	1.721(7)
Bond angles (°)					
C1–Re1–C2	89.7(3)	C11–Re11–C12	92.8(3)		
C1–Re1–C3	93.0(3)	C11–Re11–C13	92.9(3)		
C1–Re1–S1	96.6(3)	C11–Re11–S11	95.1(2)		
C1–Re1–S2	173.7(3)	C11–Re11–S12	173.5(2)		
C1–Re1–S3	91.6(3)	C11–Re11–S13	92.8(2)		
C2–Re1–C3	85.3(3)	C12–Re11–C13	85.0(3)		
C2–Re1–S1	98.4(2)	C12–Re11–S11	97.0(2)		
C2–Re1–S2	86.9(2)	C12–Re11–S12	85.8(2)		
C2–Re1–S3	178.6(2)	C12–Re11–S13	174.4(2)		
C3–Re1–S1	169.7(2)	C13–Re11–S11	171.6(2)		
C3–Re1–S2	92.0(2)	C13–Re11–S12	93.3(2)		
C3–Re1–S3	94.0(2)	C13–Re11–S13	94.3(2)		
S1–Re1–S2	78.66(6)	S11–Re11–S12	78.74(6)		
S1–Re1–S3	82.10(5)	S11–Re11–S13	82.86(6)		
S2–Re1–S3	91.84(6)	S12–Re11–S13	88.77(6)		
Re1–S1–C4	113.7(2)	Re11–S11–C14	115.1(2)		
Re1–S2–C5	114.8(2)	Re11–S12–C15	111.1(2)		
Re1–S3–C6	112.4(2)	Re11–S13–C16	111.5(2)		

Table 7
Selected bond lengths and angles in $[Re(CO)_3Br(HEt_2btu)]$ with e.s.d.s

Bond lengths (Å)					
Re–C1	1.89(1)	Re–C2	1.93(1)	Re–C3	1.95(1)
Re–O4	2.142(8)	Re–S1	2.466(2)	Re–Br	2.624(1)
S1–C4	1.71(1)	N1–C4	1.35(1)	N1–C5	1.41(1)
N2–C4	1.33(1)	N2–C6	1.47(1)	N2–C8	1.50(1)
O4–C5	1.29(1)				
Bond angles (°)					
C1–Re–C2	91.6(5)	C1–Re–C3	88.4(5)		
C1–Re–O4	173.7(4)	C1–Re–S1	92.7(3)		
C1–Re–Br	92.4(4)	C2–Re–C3	89.8(4)		
C2–Re–O4	93.6(4)	C2–Re–S1	175.4(3)		
C2–Re–Br	91.4(3)	C3–Re–O4	95.2(4)		
C3–Re–S1	91.9(3)	C3–Re–Br	178.5(3)		
O4–Re–S1	82.1(2)	O4–Re–Br	83.9(2)		
S1–Re–Br	86.82(6)	S1–C4–N1	123.0(6)		
C4–N1–C5	127.9(7)	N1–C5–O4	121.7(8)		
C5–O4–Re	131.4(6)	Re–S1–C4	106.8(3)		

Table 8
Selected bond lengths and angles in $[Re_2(CO)_6(HEt_2tcb)_2]$ with e.s.d.s

Bond lengths (Å)					
Re–C1	1.89(1)	Re–C2	1.90(1)	Re–C3	1.92(1)
Re–N2	2.155(7)	Re–S	2.507(2)	Re–S′	2.545(2)
S–C4	1.77(1)	C4–N1	1.34(1)	C4–N3	1.33(1)
N1–C5	1.34(1)	N2–C5	1.30(1)	N3–C6	1.55(2)
N3–C8	1.53(1)				
Bond angles (°)					
C1–Re–C2	89.7(4)	C1–Re–C3	88.0(4)		
C1–Re–N2	95.4(3)	C1–Re–S	94.2(3)		
C1–Re–S′	171.4(3)	C2–Re–C3	88.8(4)		
C2–Re–N2	92.5(3)	C2–Re–S	174.8(2)		
C2–Re–S′	94.7(3)	C3–Re–N2	176.4(3)		
C3–Re–S	94.8(2)	C3–Re–S′	99.4(2)		
N2–Re–S	83.7(2)	N2–Re–S′	77.1(2)		
S–Re–S′	80.97(8)	S–C4–N1	126.2(7)		
C4–N1–C5	124.8(9)	N1–C5–N2	127.0(6)		
C5–N2–Re	132.6(5)	Re–S1–Re′	99.03(8)		
Re–S–C4	115.3(2)				

Table 9
Selected bond lengths and angles in the complex anion of $(Et_4N)[Re(CO)_3Br(morphtcbph)]$ with e.s.d.s

Bond lengths (Å)					
Re–C1	1.92(1)	Re–C2	1.93(1)	Re–C3	1.95(1)
Re–N1	2.209(6)	Re–S	2.476(2)	Re–Br	2.647(2)
S–C5	1.730(8)	C5–N2	1.31(1)	C5–N3	1.36(1)
N2–C4	1.35(1)	N1–C4	1.31(1)	N1–C21	1.45(2)
C4–C11	1.51(1)	N3–C6	1.45(1)	N3–C9	1.49(1)
Bond angles (°)					
C1–Re–C2	88.9(3)	C1–Re–C3	90.9(4)		
C1–Re–N1	177.1(3)	C1–Re–S	92.0(3)		
C1–Re–Br	88.8(3)	C2–Re–C3	90.7(4)		
C2–Re–N1	93.9(3)	C2–Re–S	178.2(2)		
C2–Re–Br	93.1(2)	C3–Re–N1	90.0(3)		
C3–Re–S	90.8(3)	C3–Re–Br	176.1(3)		
N1–Re–S	85.3(2)	N1–Re–Br	90.2(2)		
S–Re–Br	85.37(7)	S–C5–N2	126.1(6)		
C5–N2–C4	129.1(7)	N2–C4–N1	125.3(7)		
C4–N1–Re	128.1(6)	Re–S1–C5	98.5(3)		

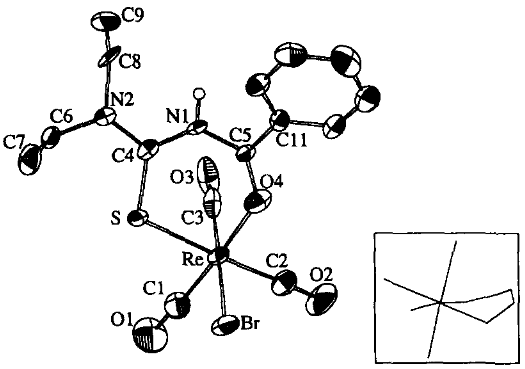

Fig. 2. ORTEP plot [17] of [Re(CO)$_3$Br(HEt$_2$btu)]. Hydrogen atoms (except that on the non-deprotonated chelating ligand) are omitted for clarity.

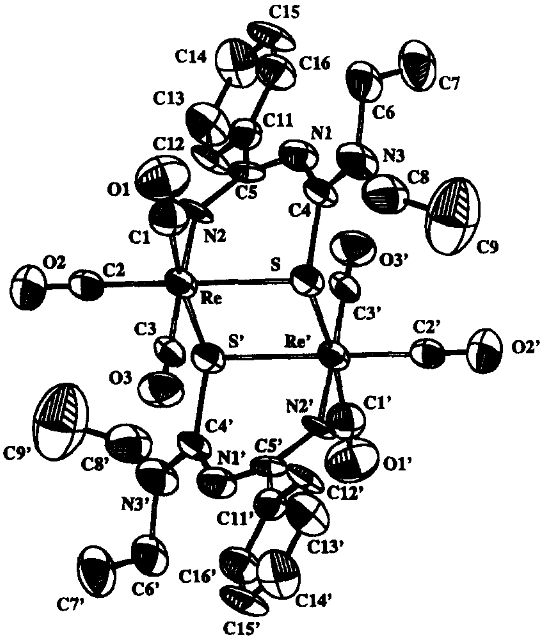

Fig. 3. ORTEP plot [17] of [Re$_2$(CO)$_6$(Et$_2$tcbH)$_2$]. Hydrogen atoms are omitted for clarity.

by inversion. The center of inversion is positioned in the center of the almost square Re$_2$S$_2$ ring. Fig. 3 shows an ORTEP plot of the dimer. Table 8 contains selected bond distances and angles. The central unit of the molecule is the four-membered Re$_2$S$_2$ ring. The Re–S bond length which forms the bridge to the neighboring metal atom is only slightly larger than that in its own *N*,*N*-dialkylthiocarbamoylbenzamidinato chelate system (2.545(2) versus 2.507(2) Å). The rhenium atoms are octahedrally coordinated with facially bonded CO ligands. An almost planar arrangement can be found for the six-membered chelate ring. All carbon–nitrogen bonds of this chelate system are equal within 0.03 Å which suggests an extended π-system

(Et$_4$N)[Re(CO)$_3$Br(morphtcbph)] forms pale yellow needles which are soluble in acetone or CH$_2$Cl$_2$. No significant shifts of the carbonyl frequencies in the IR spectrum can be detected with respect to the starting compound (Et$_4$N)$_2$[Re(CO)$_3$Br$_3$] which reflects the negative charge in this complex. Crystal suitable for X-ray crystallography could be obtained from CH$_2$Cl$_2$/iso-propanol solutions. The structure consists of well separated complex anions and tetraethylammonium cations. Fig. 4 shows an ORTEP representation of the complex anion together with the atomic labeling scheme. Selected bond distances and angles are given in Table 9. As in the other compounds, the rhenium atom has a distorted octahedral environment with three facially coordinated carbonyls. The N-phenyl-substituted thiocarbamoylbenzamidinato ligand is deprotonated and forms an almost planar chelate ring as its unsubstituted analog. A comparison of the Re–N bond lengths in both complexes shows that in [Re(CO)$_3$Br(morphtcbph)]$^-$ to be longer by 0.054(2) Å. This may be understood by the sterical demands of the phenyl group.

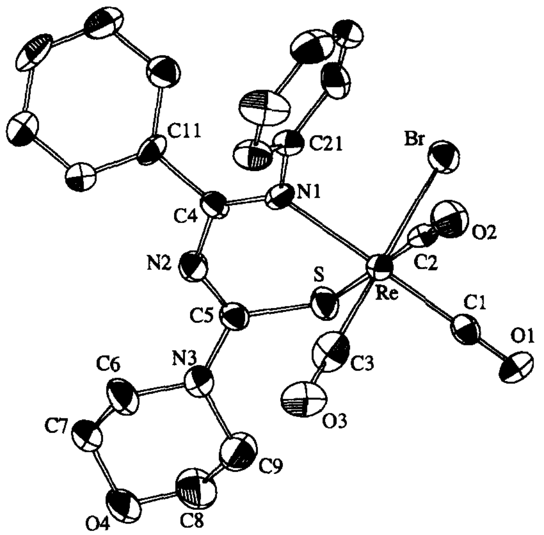

Fig. 4. ORTEP plot [17] of the complex anion in (Et$_4$N)-[Re(CO)$_3$Br(morphtcbph)]. Hydrogen atoms are omitted for clarity.

The rhenium–sulfur distances are nearly equal in the neutral [Re(CO)$_3$Br(HEt$_2$btu)] and the anionic [Re(CO)$_3$Br(morphtcbph)]$^-$ (2.466(2) and 2.476(2) Å, respectively). Somewhat longer is that in the dimeric, sulfur bridged complex (2.0507(2) Å to the chelate coordinated rhenium atom), which can be explained by the realization of three bonds to the sulfur atom. The longest Re–S bonds can be detected in the cationic complex with non-substituted thiourea (2.522(2)–2.533(2) Å). This goes along with a relatively short C–S bond which reflects the restricted possibilities of electron delocalization in this system. In summary, the Re–S bond lengths discussed in this paper are lengthened by 0.1–0.2 Å with respect to the rhenium–sulfur bonds in dialkylthiocarbamoylbenzamidinato complexes of rhenium with the metal in higher oxidation states [21–23]. This may be explained by the influence of the electron-rich rhenium(I) center but should mainly be caused by the strong *trans* labilizing acting of the carbonyl ligands.

4. Conclusions

$[Re(CO)_3Br_3]^{2-}$ is a suitable synthon for the preparation of low-valent rhenium complexes with the '*fac*-$Re(CO)_3$' unit. Thiourea is able to replace the bromo ligands and gives a cationic $[Re(CO)_3L_3]^+$ complex. Neutral and anionic complexes can be prepared using chelating thiourea derivatives with different basicity. Mono- and binuclear products are formed depending on the sterical requirements of the ligands.

5. Supplementary material

Further details of the crystal structure determinations (F_oF_c lists, full lists of bond lengths and angles, anisotropic thermal parameters, hydrogen atom positions) have been deposited with the Fachinformationszentrum, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, as Supplementary Publication Nos. CSD 400936 ($[Re(CO)_3(tu)_3](NO_3)\cdot(Et_4N)(NO_3)$, CSD 404064 ($[Re(CO)_3Br(HEt_2btu)]$), CSD 404065 ($[Re_2(CO)_6(HEt_2tcb)_2]$) and CSD 404066 ($(Et_4N)[ReBr(CO)_3(morphtcbph)]$).

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