DALTON
FULL PAPER

$[NBu_4][ReNCl_4]$: Facile synthesis, structure, electron paramagnetic resonance spectroscopy and reactions

Ulrich Abram,*[a] Martin Braun,[b] Sonja Abram,[b] Reinhard Kirmse[a] and Andreas Voigt[c]

[a] *Forschungszentrum Rossendorf, Institute of Radiochemistry, c/o Dresden University of Technology, Institute of Analytical Chemistry, D-01062 Dresden, Germany*
[b] *Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany*
[c] *Institute of Inorganic Chemistry, University of Leipzig, Talstrasse 35, D-04103 Leipzig, Germany*

The compound $[NBu_4][ReNCl_4]$ has been found to be easily accessible by the reaction of $[NBu_4][ReO_4]$ with sodium azide and HCl gas in ethanol and represents an excellent precursor for the synthesis of further rhenium nitrido complexes. It has been studied by X-ray crystallography. Rhenium(VI) compounds of the general formula $[ReNX_{4(5)}]^{-,2-}$ (X = Br or NCS) were obtained when $[NBu_4][ReNCl_4]$ reacts with HBr or KSCN. The products as well as mixed-ligand intermediates which are formed during the ligand exchange have been studied by EPR spectroscopy. The EPR parameters of the individual mixed-ligand compounds are clearly correlated to the composition of the co-ordination sphere and can be used to characterize the mixed-ligand species unambiguously. This is shown by a nearly linear dependence of g_0, $g_\parallel$, a_0^{Re} and $A_\parallel^{Re}$ on the spin–orbit coupling constants of the equatorial donors. Reactions of $[NBu_4][ReNCl_4]$ with most organic ligands yielded rhenium(V) compounds. A number of phosphine complexes and chelates with sulfur-containing ligands have been prepared and spectroscopically characterized. A crystallographic study on $[ReN(Hdetcb)_2]$ ($Hdetcb^- = N^2$-diethylthiocarbamoylbenzamidinate) shows *cis* co-ordination for the chelating S,N-donor ligands. Weak intermolecular hydrogen bridges have been found between the co-ordinated nitrogen atoms and the lone pair of the nitrido nitrogen. A comparison between the crystal structural data of $[NBu_4]_2[ReN(mnt)_2]$ (mnt^{2-} = 1,2-dicyanoethene-1,2-dithiolate), prepared from $[NBu_4][ReNCl_4]$ and Na_2mnt, and $[NBu_4][ReO(mnt)_2]$ shows longer Re–S bonds in the nitrido anion but markedly higher O–Re–S bond angles indicating higher steric requirements of the oxo ligand compared with 'N^{3-}'.

The tetrachloronitridorhenate anion, $[ReNCl_4]^-$, was first prepared about 20 years ago by reaction of the neutral rhenium(VII) nitride chloride $ReNCl_4$ with tetraphenylarsonium chloride.[1] The compound has been fully characterised, its crystal structure elucidated[2] and ligand-exchange reactions with Br^- and NCS^- reported which lead to the rhenium(VI) anions $[ReNBr_4]^-$ and $[ReN(NCS)_5]^{2-}$.[3,4] For a large-scale synthesis, however, the approach *via* the neutral rhenium nitride chlorides $ReNCl_3$ or $ReNCl_4$ [equations (1) and (2)] seems to

$$ReNCl_3 + AsPh_4Cl \longrightarrow [AsPh_4][ReNCl_4] \qquad (1)$$

$$ReNCl_4 + AsPh_4Cl \longrightarrow [AsPh_4][ReNCl_4] + \tfrac{1}{2}Cl_2 \qquad (2)$$

be less appropriate with regard to their syntheses from $ReCl_5$ and nitrogen trichloride and chlorine azide, respectively.[1,5] The reaction of $[ReCl_4(NSCl)(POCl_3)]$ with $AsPh_4Cl$ [equation (3)]

$$[ReCl_4(NSCl)(POCl_3)] + AsPh_4Cl \longrightarrow [AsPh_4][ReNCl_4] + POCl_3 + SCl_2 \qquad (3)$$

avoids the use of these vigorous reagents, but the rhenium starting material has to be prepared in a multistep synthesis from $ReCl_5$ and trithiazyl chloride $(SNCl)_3$.[6–8] Therefore, commonly the triphenylphosphine complex $[ReNCl_2(Ph_3P)_2]$, which can be prepared in good yields from $[ReOCl_3(Ph_3P)_3]$ and phenylhydrazine[9] or from perrhenate, aqueous HCl, NaN_3 and Ph_3P,† is used as precursor for the synthesis of nitridorhenium compounds.[10–14] However, the presence of Ph_3P in the co-ordination sphere of the metal and particularly its low solubility in most common solvents restrict the applicability of this starting material.

In the present paper we describe a facile synthesis of $[NBu_4][ReNCl_4]$ from perrhenate, sodium azide and HCl. Its crystal structure and a detailed analysis of the EPR spectra of the d^1 system are reported. We demonstrate that $[ReNCl_4]^-$ is a suitable starting material for the synthesis of new rhenium nitrido complexes and discuss the structures of the neutral $[ReN(Hdetcb)_2]$ ($Hdetcb^- = N^2$-diethylthiocarbamoylbenzamidinate) and of the complex anion $[ReN(mnt)_2]^{2-}$ (mnt^{2-} = 1,2-dicyanoethene-1,2-dithiolate). The structure of $[ReN(mnt)_2]^{2-}$ is compared with that of its oxo analogue $[ReO(mnt)_2]^-$.

Results and Discussion

Tetrachloronitridorhenate(VI) can be prepared in good yields in a single-pot synthesis from tetrabutylammonium perrhenate, HCl gas and sodium azide. The synthesis follows a general route for the preparation of tetrahalogenonitridometalates[10,11] and has also been applied for the lighter equivalent of rhenium. Baldas *et al.*[15] demonstrated that $[TcNCl_4]^-$ and $[TcNBr_4]^-$ can be prepared from pertechnetate and sodium azide in excellent yields even in hot aqueous HCl or HBr without any hydrolysis. The anionic complexes can easily be precipitated with bulky cations. When the same protocol is applied to rhenium, a mixture of mainly rhenium-(IV) and -(V) compounds is obtained and $[ReNCl_4]^-$ is only formed as a minor side-product. To increase the amount of the nitrido complex it is necessary to keep the temperature of the reaction mixture low and to add several small portions of azide rather than one big amount. When the reaction is interrupted after addition of the first

---

† The synthesis of $[ReNCl_2(Ph_3P)_2]$ *via* the reaction $ReO_4^- + N_3^- + HCl(aq) + Ph_3P + EtOH \longrightarrow [ReNCl_2(Ph_3P)_2]$ was suggested by one of the referees and works well.

portion of azide considerable amounts of ReO_4^- and $[ReOCl_4]^-$ are observed.

The mechanism of the reaction is not completely clear. The assumption in ref. 15 that the $[MNX_4]^-$ anions are finally formed *via* a metal(IV) transition state is sound with regard to the fact that the formation of a nitrido function from a co-ordinated azide requires a two-electron oxidation of the metal. Attempts to isolate $[TcNCl_4]^-$ or $[ReNCl_4]^-$ from isolated hexachlorometalates(IV), however, gave unsatisfactory results with only small amounts of impure technetium(VI) or rhenium(VI) complexes.[16] On the other hand, tetrachloronitridotechnetate(VI) can be isolated in good yields from $[TcOCl_4]^-$ (refs. 17 and 18) which is the product of the reaction of TcO_4^- with HCl at ambient temperature. This suggests an intermediate formation of the unstable technetium(VII) nitrido compound which is rapidly reduced by Cl^- to give the very stable $Tc^{VI}N$ core. It is the extraordinary stability of the TcN core (which even resists an aqueous hydrolysis[19] or reactions with H_2O_2[20,21]) which makes the one-step synthesis of $[TcNCl_4]^-$ possible. For the synthesis of pure $[ReNCl_4]^-$, however, several portions of azide must be added subsequently. Obviously, the intermediately formed rhenium(VII) compound ($ReNCl_4$ or $[ReNCl_5]^-$) is less resistant to acidic hydrolysis than its technetium analogue and/or the higher reduction potential of Re^{VII} prevents a rapid reduction to Re^{VI} and prefers hydrolysis. Thus, considerable amounts of perrhenate are reformed which react with the HCl gas to give $[ReOCl_4]^-$ and, thus, are transferred back to the formation of the nitrido complex when more azide is provided. Usually, three additions of sodium azide are sufficient to obtain $[NBu_4][ReNCl_4]$ in good yields and high purity. The absence of the possible impurities $[NBu_4][ReO_4]$ and $[NBu_4][ReOCl_4]$ can easily be checked by IR spectroscopy. The ν(Re≡N) vibration at 1103 cm^{-1} is well separated from the regions where the Re=O frequencies of $[ReOCl_4]^-$ (1033 cm^{-1}) and ReO_4^- (913 cm^{-1}) can be detected.

The caesium salt $Cs_2[ReNCl_5]$ precipitates on addition of CsCl to the reaction mixture described above. The complex anion is six-co-ordinate. This is in accordance with the situation in other oxo- or nitrido-metalates with halide ligands, where with alkali-metal cations preferably $[MYX_5]^{2-}$ anions (Y = N or O, X = Cl or Br) are precipitated from solutions which contain excess of X^-, whereas $[MYX_4]^-$ or $[MYX_4(solv)]^-$ are preferred with large organic cations.[22] The compound $Cs_2[ReNCl_5]$ is a yellow solid which is stable in air, but more sensitive to hydrolysis than the tetrabutylammonium salt. The Re≡N frequency of the six-co-ordinate compound is found at 1053 cm^{-1}. The use of $Cs_2[ReNCl_5]$ for ligand exchange is particularly useful when strong ligands are used and water is required as solvent.

Sodium azide can be replaced by $SiMe_3N_3$ in the formation of $[NBu_4][ReNCl_4]$. This allows one to work in dichloromethane. Using this approach the reformation of ReO_4^- can be minimized by careful drying of the solvent. The overall yield of the nitrido complex, however, is less than when using several portions of sodium azide.

The compound $[NBu_4][ReNCl_4]$ is air-stable and does not hydrolyse under ambient conditions. In water, however, a black-brown, insoluble solid is rapidly formed. When this product is treated with HCl or $SOCl_2$ only a few percent can be retransferred to $[ReNCl_4]^-$. The same can be observed during the hydrolysis of $Cs_2[ReNCl_5]$ which undergoes disproportionation to ReO_4^- and insoluble rhenium(IV) species when treated with water.

The compound $[NBu_4][ReNCl_4]$ crystallises in the tetragonal space group *P*4/*n* and the anion (see Fig. 1) shows the expected C_{4v} symmetry. The Re–N and Re–Cl bond lengths of 1.612(8) and 2.323(1) Å are the same as observed in the tetraphenylarsonium salt.[2] The Re–N distance is consistent with a rhenium–nitrogen triple bond. There are no exceptional bonding features for the tetrabutylammonium cation.

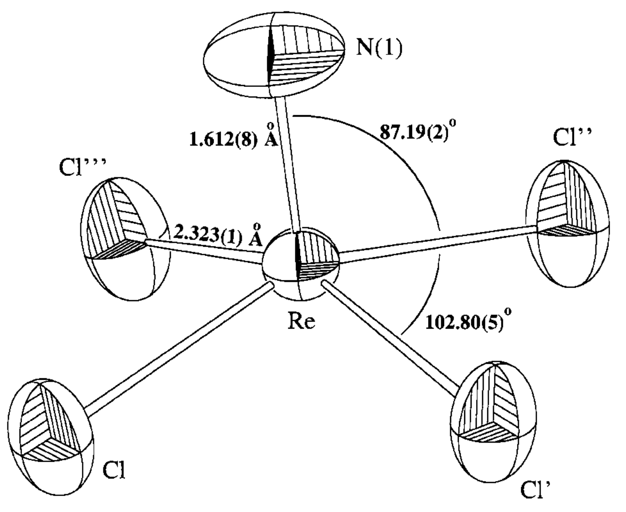


Fig. 1 Molecular structure of the complex anion in $[NBu_4][ReNCl_4]$ together with the bond lengths and angles [symmetry codes (′) 0.5 − *y*, *x*, *z*; (″) 0.5 − *x*, 0.5 − *y*, *z*; (‴) 0.5 − *x*, 0.5 − *y*, *z*]. The thermal ellipsoids represent 50% probability[23]

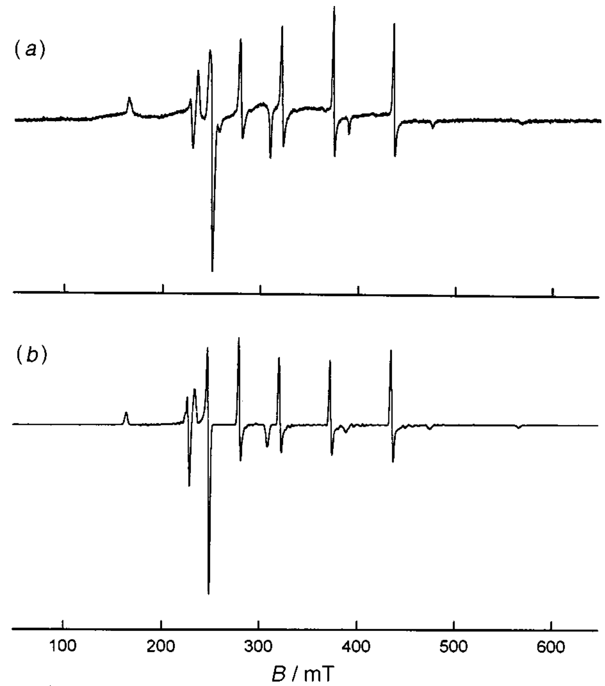


Fig. 2 (*a*) Experimental X-band EPR spectrum of $[AsPh_4]_2[ReN(NCS)_5]$ in CH_2Cl_2, *T* = 130 K. (*b*) Simulated spectrum

Rhenium(VI) compounds of the type $[ReNX_{4(5)}]^{-,2-}$ (X = Cl, Br or NCS) are favoured for EPR studies because of their $5d^1$ ($S = \frac{1}{2}$) configuration. The spectra of the parent complexes $[ReNCl_{4(5)}]^{-,2-}$ and $[ReNBr_4]^-$ are known.[24,25] As found for the nitridorhenium compounds $[ReNX_{4(5)}]^{-,2-}$ (X = Cl or Br) the $[ReN(NCS)_5]^{2-}$ species gives a well resolved room-temperature X-band EPR spectrum consisting of six $^{185,187}Re$ hyperfine structure (h.f.s.) lines. This sextet arises from the interaction of the unpaired electron with the nuclear spin of both rhenium isotopes ^{185}Re and ^{187}Re ($I^{Re} = \frac{5}{2}$; natural abundance ^{185}Re 37.4% and ^{187}Re 62.6%). The frozen-solution EPR spectrum of $[AsPh_4]_2[ReN(NCS)_5]$ and its simulation are reproduced in Fig. 2. This spectrum shows a typical axially symmetric pattern with six $^{185,187}Re$ h.f.s. lines in the parallel and the perpendicular part. For the spectrum at *T* = 130 K as well as for the room-temperature spectrum, ligand h.f.s. splittings were not resolved because of the comparatively large linewidth of ΔB_{pp} = 9–19 mT. Owing to the magnitude of the $^{185,187}Re$ h.f.s. coupling

Table 1 Experimentally obtained[a] and calculated[b] EPR parameters (g_0, $g_\parallel$, a_0^{Re} and $A_\parallel^{Re}$) for $[ReNBr_{4-p}Cl_p]^-$ mixed-ligand complexes. Hyperfine couplings are given in 10^{-4} cm^{-1}; solvent CH_2Cl_2 ($T = 295$ K) or MeCN ($T = 130$ K)

	g_0		a_0^{Re}	
Compound	Found	Calculated	Found	Calculated
$[ReNBr_4]^-$	2.005	2.005	447	447
$[ReNBr_3Cl]^-$	1.984	1.984	461	464
$[ReNBr_2Cl_2]^-$	1.962	1.964	483	480
$[ReNBrCl_3]^-$	1.944	1.944	494	497
$[ReNCl_4]^-$	1.924	1.924	513	513

	$g_\parallel$		$A_\parallel^{Re}$	
	Found	Calculated	Found	Calculated
$[ReNBr_4]^-$	2.069	2.069	665	665
$[ReNBr_3Cl]^-$	2.034	2.029	695	694
$[ReNBr_2Cl_2]^-$	1.994	1.988	721	720
$[ReNBrCl_3]^-$	1.944	1.948	744	745
$[ReNCl_4]^-$	1.908	1.908	768	768

[a] Experimental error: g_0, $g_\parallel \pm 0.003$; a_0^{Re}, $A_\parallel^{Re} \pm 3$. [b] By using $y([ReNBr_{4-p}Cl_p]^-) = \frac{1}{4}\{(4 - p)y([ReNBr_4]^-) + py([ReNCl_4]^-)\}$ with $y = g_0$, $g_\parallel$, a_0^{Re} or $A_\parallel^{Re}$.

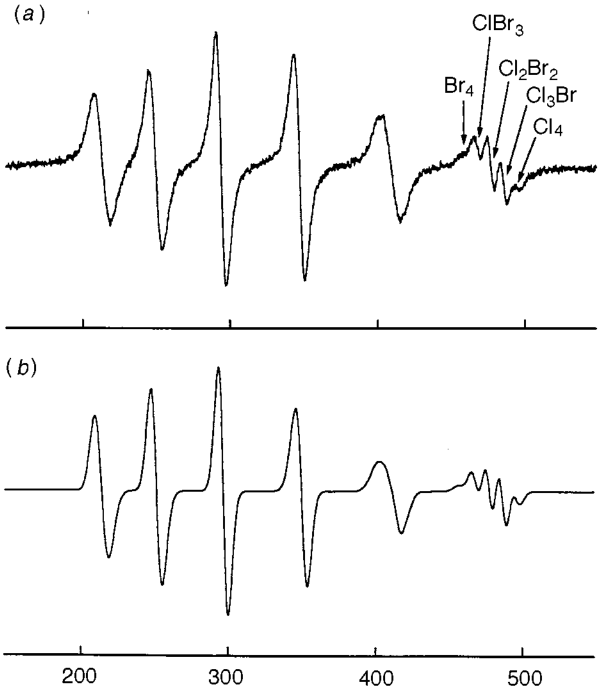


Fig. 3 (*a*) Experimental X-band EPR spectrum of $[ReNBr_{4-p}Cl_p]^-$ ($p = 0$–4) complexes in CH_2Cl_2, $T = 295$ K. The well resolved high-field line ($m_I^{Re} = +\frac{5}{2}$) shows the presence of all three possible mixed-ligand species and the parent compounds. (*b*) Simulated spectrum

constants and the nuclear quadrupole moments in both cases the equidistance of the h.f.s. lines is disturbed.

Rhenium(VI) compounds of the general formula $[ReNX_{4(5)}]^{-,2-}$ (X = Cl, Br or NCS) can be described by the spin Hamiltonian (4). All symbols have their usual meanings. The

$$H_{sp} = g\cdot\mu_B\cdot S\cdot B_0 + S\cdot A^{Re}\cdot I^{Re} + I^{Re}\cdot Q^{Re}\cdot I^{Re} \qquad (4)$$

obtained principal values of the g tensors and the $^{185,187}Re$ h.f.s. tensors A^{Re} for $[AsPh_4]_2[ReN(NCS)_5]$ are $g_\parallel = 1.817$, $g_\perp = 1.958$, $g_{av} = 1.911$, $A_\parallel^{Re} = 681.1 \times 10^{-4}$ cm^{-1}, $A_\perp^{Re} = 379.1 \times 10^{-4}$ cm^{-1} and $A_{av}^{Re} = 479.9 \times 10^{-4}$ cm^{-1} ($g_\parallel$, $g_\perp \pm 0.003$; $A_\parallel^{Re}$, $A_\perp^{Re} \pm 3.0 \times 10^{-4}$ cm^{-1}). The values for $[NBu_4][ReNCl_4]$ and $[NBu_4][ReNBr_4]$ are summarized in Table 1.

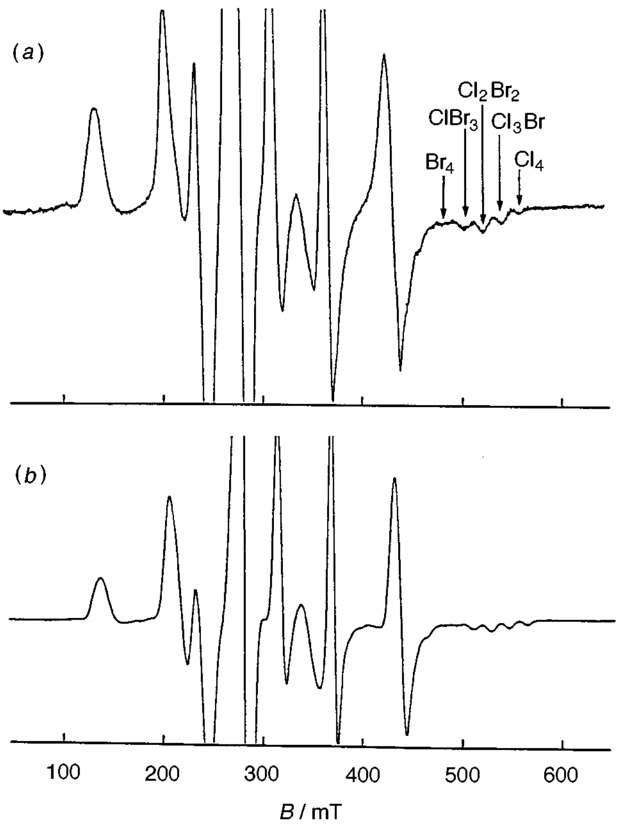


Fig. 4 (*a*) Experimental X-band EPR spectrum of $[ReNBr_{4-p}Cl_p]^-$ ($p = 0$–4) complexes in MeCN, $T = 130$ K. In the high-field region of the parallel part all three mixed-ligand species and the parent compounds are detected. (*b*) Simulated spectrum

As mentioned above the room-temperature EPR spectra of $[ReNCl_4]^-$ and $[ReNBr_4]^-$ consist of six h.f.s. lines. In the spectra of $[ReNCl_4]^-$–$[ReNBr_4]^-$ mixtures in addition to the signals of the parent compounds there are several new signals which indicate the formation of mixed-ligand complexes of the type $[ReNBr_{4-p}Cl_p]^-$ with $p = 1$–3. A typical spectrum revealing the formation of $Re^{VI}N$ mixed-ligand complexes is shown in Fig. 3. In contrast to the EPR investigation of the ligand-exchange reaction on the related nitridotechnetium compounds $[TcNX_4]^-$ (X = C or Br),[26] only the high-field line ($m_I^{Re} = \frac{5}{2}$) is clearly split. Owing to the comparatively large linewidth of $\Delta B_{pp} \approx 7$ mT for the remaining lines, the signals of the individual complexes nearly coincide, which complicates the spectral analysis. Therefore, the EPR parameters of the individual spectra were obtained by simulation. They are listed in Table 1 together with the values of their parent compounds.

In frozen-solution spectra of $[ReNCl_4]^-$–$[ReNBr_4]^-$ mixtures, in addition to the signals of the parent complexes, new signals are to be seen in the high-field region of the parallel part which must be attributed to rhenium(VI) mixed-ligand species as found in the liquid-solution spectra. A typical spectrum is shown in Fig. 4. The perpendicular part of the spectrum is very complex due to many overlappings; therefore, no attempts have been made to derive the parameters $g_\perp$ and $A_\perp^{Re}$. The $g_\parallel$ and $A_\parallel^{Re}$ of the parallel part of the spectra are listed also in Table 1. Ligand h.f.s. due to the interaction of the unpaired electron with the $^{35,37}Cl$, $^{79,81}Br$ and ^{14}N nuclei were not resolved.

The investigation of ligand-exchange reactions by means of EPR spectroscopy requires knowledge about the dependence of the EPR parameters on the type (composition, symmetry) of the co-ordination sphere. Extensive investigations have been made *e.g.* for the d^1 systems CrO^{3+}, MoO^{3+}, WO^{3+}, VO^{2+} and on related nitridotechnetium(VI) compounds of general formula $[TcNX_4]^-$ (X = Cl or Br).[26,27] According to the study on the $Tc^{VI}N$ complexes, a nearly linear dependence of the EPR

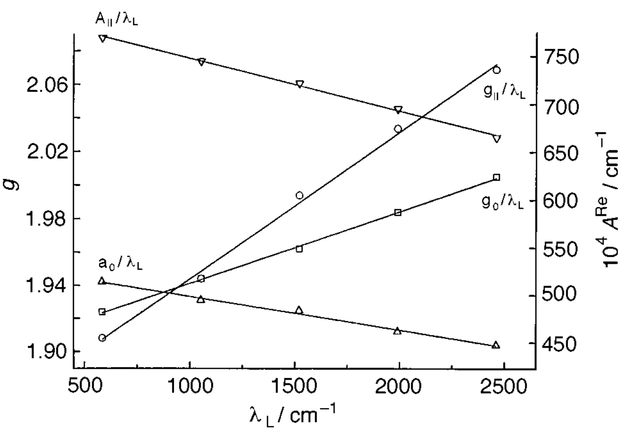


Fig. 5 Dependence of g_0, $g_\parallel$, a_0^{Re} and $A_\parallel^{Re}$ of $[ReNBr_{4-p}Cl_p]^-$ (p = 0–4) species on the effective spin–orbit coupling $\lambda_L = \frac{1}{4}[(4-p)\lambda_{Br} + p\lambda_{Cl}]$. λ_{Cl} = 586 cm^{-1} and λ_{Br} = 2460 cm^{-1}

spectral quantities, g_0, $g_\parallel$, a_0^{Re} and $A_\parallel^{Re}$ on the 'heaviness' of the first co-ordination sphere is expected. This can be defined for the present $[ReNBr_{4-p}Cl_p]^-$ complexes with p = 0–4 as in equation (5) where λ_{Cl}, λ_{Br} and λ_{Re} are the spin–orbit coupling constants of chlorine, bromine and rhenium, respectively.

$$g_0,\ g_\parallel,\ a_0^{Re},\ A_\parallel^{Re} \approx \lambda_L/\lambda_{Re} = \tfrac{1}{4}[p\lambda_{Cl} + (4-p)\lambda_{Br}]/\lambda_{Re} \qquad (5)$$

The proportionality [equation (5)] holds true if there are no significant differences concerning the structure and bonding properties of the complexes considered. Thus, if the g values and the h.f.s. coupling parameters A^{Re} of the parent complexes are known the g_0, $g_\parallel$, a_0^{Re} and $A_\parallel^{Re}$ values of the mixed-ligand complexes can be estimated simply by using the 'additivity rule' given in equation (6), with $y = g_0$, $g_\parallel$, a_0^{Re} or $A_\parallel^{Re}$. In Table 1

$$y = ([ReNBr_{4-p}Cl_p]^-) = \tfrac{1}{4}\{(4-p)y([ReNBr_4]^-) + py([ReNCl_4]^-)\} \qquad (6)$$

the g_0, $g_\parallel$, a_0^{Re} and $A_\parallel^{Re}$ values estimated for $[ReNBr_{4-p}Cl_p]^-$ mixed-ligand complexes with p = 1–3 according to equation (6) are compared with the experimentally derived ones. It can be seen that the experimental values are well reproduced by equation (6). Fig. 5 illustrates the nearly linear dependence of the observed EPR quantities of the $[ReNBr_{4-p}Cl_p]^-$ complexes with p = 0–4 on the composition of the first co-ordination sphere.

It should be noted that in solution the co-ordination of a sixth ligand X (X = Cl, Br or solvent) in *trans* position to the nitrogen may occur. However, according to several studies made on other d^1 systems the influence of a *trans*-co-ordinated ligand in the species of general formula $[ReNBr_{4-p}Cl_pX]^-$ (X = Cl, Br or solvent) with p = 0–4 should be vanishingly small.[26,27]

The EPR spectroscopically detected ligand exchange demonstrates that $[ReNCl_4]^-$ is a suitable starting material for the synthesis of rhenium nitrido complexes. The oxidation state '+6' is maintained during the reaction with halides and NCS$^-$. With excess of organic ligands reduction to rhenium(V) complexes can be observed. The previously reported formation of the rhenium(VI) species with co-ordinated Ph_3P, bipyridine (bipy) and pyridine (py)[28] obviously results from the very mild conditions applied and is in good agreement with our observations that rhenium(VI) species with co-ordinated organic ligands can also be detected by EPR spectroscopy when an only small excess of ligand is used. Similar observations could be made for technetium, where the crystal structure of $[TcNCl_3(bipy)]$[29] has been elucidated and EPR spectra of technetium(VI) species with co-ordinated Ph_3P and Ph_3As ligands have been reported.[30]

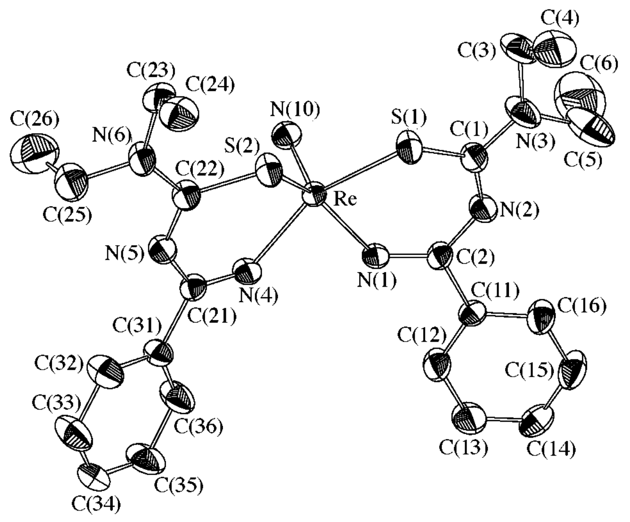
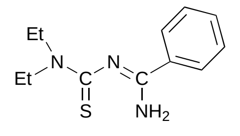
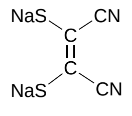


Fig. 6 Molecular structure of $[ReN(Hdetcb)_2]$ along with the atomic numbering scheme (thermal ellipsoids represent 50% probability)[23]

Besides of reactions of $[NBu_4][ReNCl_4]$ with Ph_3P, Me_2PhP and diethyldithiocarbamate ($S_2CNEt_2^-$) which gave the previously reported rhenium(V) complexes $[ReNCl_2(Ph_3P)_2]$, $[ReNCl_2(Me_2PhP)_3]$ and $[ReN(S_2CNEt_2)_2]$,[31] we attempted reactions with N^2-diethylthiocarbamoylbenzamidine (H_2detcb) and sodium 1,2-dicyanoethene-1,2-dithiolate (Na_2mnt). Our recent attempts to isolate crystalline samples of $[ReN(Hdetcb)_2]$ and $[ReN(mnt)_2]^{2-}$ from reactions of $[ReNCl_2(Ph_3P)_2]$ or $[ReNCl_2(Me_2PhP)_3]$ failed. In the former case only oily products were obtained and in the latter case the ligand exchange stopped at the stages $[ReN(Cl)(Me_2PhP)_2(Hdetcb)]$[32] and $[ReN(Me_2PhP)_2(mnt)]$,[33] respectively. The structures of both products have been solved.[32,34] With $[NBu_4][ReNCl_4]$, however, $[ReN(Hdetcb)_2]$ and $[NBu_4]_2[ReN(mnt)_2]$ could be easily isolated and structurally characterized.



H_2detcb



Na_2mnt

The compound $[ReN(Hdetcb)_2]$ is an orange-red solid which crystallizes directly from $[ReNCl_4]^-$–H_2detcb–Et_3N reaction mixtures. It is readily soluble in $CHCl_3$ and CH_2Cl_2, but only slightly soluble in alcohols. The NMR and mass spectra are in agreement with the formulation of a five-co-ordinate rhenium(V) complex with two $Hdetcb^-$ ligands. This is confirmed by the crystal structure. Fig. 6 shows an ellipsoid representation of the molecular structure along with the atomic labeling scheme. Selected bond lengths and angles are contained in Table 2. The rhenium atom has a distorted square-pyramidal co-ordination sphere with the nitrido nitrogen at the apical position. The metal is displaced by 0.511(3) Å from the basal plane which is formed by the donor atoms of the chelating ligands. In accordance with other rhenium nitrido complexes, the Re≡N bond is short [1.657(4) Å]. Almost equal lengths (≈1.33 Å) are observed for all C–N bonds in the chelate ring systems. This also includes the C–N bonds between the diethylamino substituents and the chelate rings [C(1)–N(3) 1.343(7), C(22)–N(6) 1.344(6) Å], indicating a noticeable deviation from a normal single C–N bond length of the latter and the presence of an extended conjugated π system.

The bond lengths of the equatorial donors are longer by a mean value of about 0.05 Å compared with the situation in the corresponding cationic oxo complex $[ReO(Hdetcb)_2]^+$.[35] In both compounds the thiocarbamoylbenzamidinates are *cis* co-ordinated. The same has been found previously for the corre-

Table 2 Selected bond lengths (Å) and angles (°) in [ReN(Hdetcb)$_2$]

Re–N(10)	1.657(4)	Re–N(1)	2.076(4)
Re–S(1)	2.355(1)	Re–N(4)	2.063(4)
Re–S(2)	2.350(1)	S(1)–C(1)	1.741(5)
C(1)–N(2)	1.324(6)	N(2)–C(2)	1.335(6)
C(2)–N(1)	1.309(6)	S(2)–C(22)	1.744(5)
C(22)–N(5)	1.324(6)	N(5)–C(21)	1.333(6)
N(4)–C(21)	1.323(6)	H(1)–N(10′)	2.416(9)
H(4)–N(10′)	2.481(9)		
N(10)–Re–S(1)	105.5(2)	N(10)–Re–N(1)	105.9(2)
N(10)–Re–S(2)	107.2(2)	N(10)–Re–N(4)	104.2(2)
S(1)–Re–N(1)	88.5(1)	S(1)–Re–S(2)	81.93(5)
S(1)–Re–N(4)	150.3(1)	S(2)–Re–N(4)	88.3(1)
S(2)–Re–N(1)	146.8(1)	N(1)–Re–N(4)	84.5(2)
Re–S(1)–C(1)	106.9(2)	S(1)–C(1)–N(2)	127.4(4)
C(1)–N(2)–C(2)	127.7(4)	N(2)–C(2)–N(1)	127.7(4)
C(2)–N(1)–Re	132.2(3)	Re–S(2)–C(22)	105.6(2)
C(22)–N(5)–C(21)	127.3(4)	N(5)–C(21)–N(4)	126.6(4)
C(21)–N(4)–Re	132.6(3)	N(1)–H(1)–N(10′)	148.4(8)
N(4)–H(4)–N(10′)	148.4(8)		

Symmetry code: (′) −*x*, 1 − *y*, −*z*.

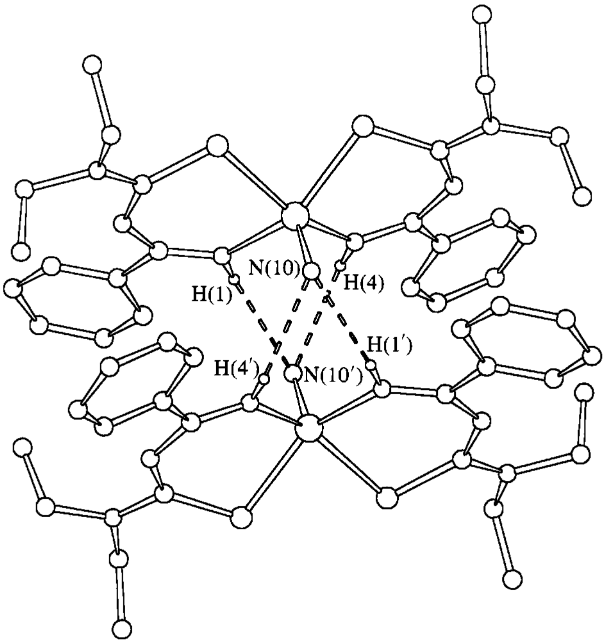


Fig. 7 Structure representation[38] of [ReN(Hdetcb)$_2$] showing the association of two molecules by weak hydrogen bridges

sponding technetium complexes.[36,37] For the oxo compounds this result can easily be explained by the presence of hydrogen bridges between the remaining H atoms of the singly deprotonated benzamidinate sites and the Cl$^-$ anion in [TcO(Hdetcb)$_2$]Cl[35] and a cocrystallized OPPh$_3$ molecule in [ReO(Hdetcb)$_2$][BPh$_4$]·OPPh$_3$.[35] The packing diagram of [ReN(Hdetcb)$_2$] shown in Fig. 7 indicates weak dimeric interactions. The H atoms of the *cis* co-ordinated thiocarbamoylbenzamidinate ligands are strictly oriented towards the terminal nitride ligand of the neighbouring molecule. The distances between these H atoms (which have been located in the Fourier maps) and the nitrido function of approximately 2.5 Å suggest at least weak hydrogen bridges. This structural result is supported by the IR frequency of the NH bond at 3270 cm^{-1} in [ReN(Hdetcb)$_2$] which lies between the values found for [ReO(Hdetcb)$_2$][BPh$_4$]·OPPh$_3$ (3210 cm^{-1})[35] and [ReN(Cl)(Me$_2$PhP)$_2$(Hdetcb)] (3318 cm^{-1}).[32]

Table 3 Selected bond lengths (Å) and angles (°) in the complex anions of [NBu$_4$]$_2$[ReN(mnt)$_2$] and [NBu$_4$][ReO(mnt)$_2$]

	[NBu$_4$]$_2$[ReN(mnt)$_2$]	[NBu$_4$][ReO(mnt)$_2$]
Re–N/O(10)	1.653(5)	1.668(4)
Re–S(1)	2.358(2)	2.322(2)
Re–S(2)	2.354(2)	2.316(2)
Re–S(3)	2.361(2)	2.307(2)
Re–S(4)	2.354(2)	2.311(2)
S(1)–C(1)	1.732(7)	1.755(6)
C(1)–C(2)	1.34(1)	1.337(8)
S(2)–C(2)	1.742(8)	1.751(6)
S(3)–C(5)	1.741(8)	1.730(6)
C(5)–C(6)	1.34(1)	1.336(8)
S(4)–C(6)	1.768(8)	1.749(6)
N/O(10)–Re–S(1)	105.4(2)	107.4(2)
N/O(10)–Re–S(2)	106.4(2)	110.1(2)
N/O(10)–Re–S(3)	104.5(2)	107.5(2)
N/O(10)–Re–S(4)	106.9(2)	107.7(2)
S(1)–M–S(2)	85.46(7)	85.28(6)
S(1)–M–S(3)	150.1(1)	145.11(6)
S(1)–M–S(4)	85.76(7)	84.01(7)
S(2)–M–S(3)	86.34(7)	82.95(6)
S(2)–M–S(4)	146.67(8)	142.23(7)
S(3)–M–S(4)	85.50(7)	85.48(6)

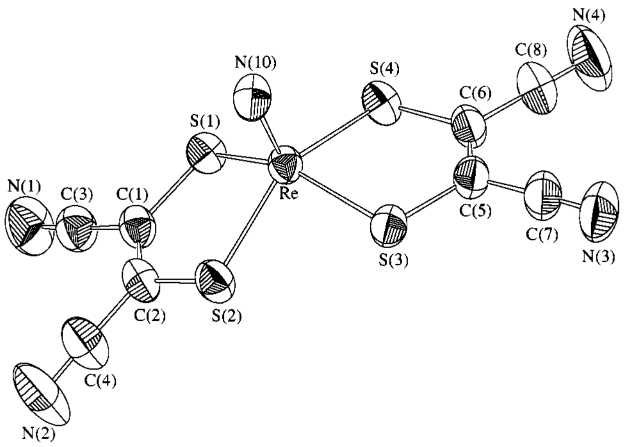
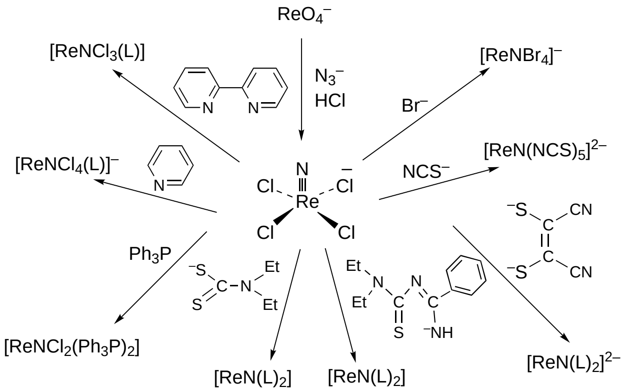


Fig. 8 Molecular structure of the complex anion in [NBu$_4$]$_2$[ReN(mnt)$_2$] along with the atomic numbering scheme (thermal ellipsoids represent 30% probability). The atom numbering is also valid for the [ReO(mnt)$_2$]$^-$ anion; bond distances and angles are given in Table 3

Yellow crystals of [NBu$_4$]$_2$[ReN(mnt)$_2$] are obtained when [NBu$_4$][ReCl$_4$] is treated with Na$_2$mnt. The IR spectrum of the compound shows strong absorptions at 2198 and 1056 cm^{-1} due to the C≡N and Re≡N vibrations. The negative mode FAB mass spectrum is characterized by many metal-containing fragments. A peak at *m*/*z* = 723 is due to the ion pair {[NBu$_4$][ReN(mnt)$_2$]}$^-$. No evidence could be found for the dianion [ReN(mnt)$_2$]$^{2-}$. This is in accordance with mass spectrometric studies on other diionic transition-metal complexes, where only monoionic complexes could be detected applying positive-ion FAB ionization on dicationic technetium complexes[39] or during a negative-ion FAB study on [TcN(i-mns)$_2$]$^{2-}$ (i-mns = 1,1-dicyanoethene-2,2-diselenolate).[40] The fragmentation of the [ReN(mnt)$_2$]$^-$ anion is characterized by the loss of sulfur and the abstraction of complete mnt ligands.

The crystal structure of [NBu$_4$]$_2$[ReN(mnt)$_2$] consists of well separated [ReN(mnt)$_2$]$^{2-}$ anions and NBu$_4^+$ cations. Fig. 8 shows an ORTEP representation of the complex ion. Corresponding bond lengths and angles are summarized in Table 3. The rhenium is five-co-ordinate with the nitrido nitrogen at the apex of a distorted square pyramid. The basal plane of this pyramid is formed by the sulfur atoms of the mnt ligands. The Re atom is situated about 0.642(1) Å out of this plane towards the 'N^{3-}' ligand. The Re≡N bond is short [1.653(5) Å] as is expected for a triple bond. The mnt ligands are planar within 0.141(1) and 0.178(1) Å, respectively. An angle of 33.14(9)° is formed between these two planes.



Scheme 1

For comparison purposes, the analogous rhenium(V) oxo complex $[NBu_4][ReO(mnt)_2]$ has been prepared from $[NBu_4][ReOCl_4]$ and Na_2mnt. The compound forms well shaped orange-brown plates. The crystal structure shows complex anions with square-pyramidally co-ordinated rhenium atoms and tetrabutylammonium cations. The structure of the $[ReO(mnt)_2]^-$ anion is visually the same as that of $[ReN(mnt)_2]^{2-}$. Since there are no unusual thermal ellipsoids which would justify a separate reproduction of the oxo anion, the structural drawing is omitted. Selected bond lengths and angles, however, are contained in Table 3 and are compared with the corresponding values in the nitrido complex. The atom labelling scheme in the oxo anion is identical with that in $[ReN(mnt)_2]^{2-}$. It is obvious that the Re–S bonds are somewhat longer in the nitrido compound. This goes along with smaller angles between the 'N^{3-}' ligand and the equatorial donors and consequently the displacement of Re from the square basal or equatorial plane is greater for the oxo complex [0.721(1) *vs.* 0.642(1) Å]. The same findings could be derived for a number of five-co-ordinate TcN/TcO couples with identical equatorial ligands (including complexes with the metal in the oxidation states '+5' and '+6' [15,40–47]). The reason for these results may be attributed to a greater structural steric effect of the oxo ligand and the lower core charge of 'MN^{2+}' *vs.* 'MO^{3+}'. Other pairs of structurally identical five-co-ordinate oxo- and nitrido-rhenium complexes are not available for comparison. However, similar results can be found when the bonding situations in the six-co-ordinate couple $[Re^{VI}N(NCS)_5]^-$–$[Re^{V}O(NCS)_5]^-$ are compared.[4,48] Additionally, a stronger *trans* influence is detected for the nitride ligand by a longer rhenium-(*trans*) nitrogen bond length.

Conclusion

The anion $[ReNCl_4]^-$ can be prepared in a facile synthesis from perrhenate, sodium azide and HCl gas. The composition of the mixed-ligand complexes of the general formula $[ReNBr_{4-p}Cl_p]^-$ with $p = 1–3$ obtained by the reaction between $[ReNCl_4]^-$ and $[ReNBr_4]^-$ can easily be determined by means of EPR spectroscopy, which is found to be dependent in a characteristic manner on the composition of the complexes. The complex $[NBu_4][ReNCl_4]$ is a reactive starting material for the synthesis of rhenium-(VI) and -(V) complexes. This has been demonstrated with a variety of ligands having different donor atom sets. A summary is given in Scheme 1. Reactions with multidentate ligands are currently being investigated in our laboratories.

Experimental

The NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AM400 spectrometer with $SiMe_4$ as internal standard, FAB mass spectra on a MAT 701A spectrometer (Finnigan, with xenon as primary beam gas, the ion gun operated at 8 kV and 100 μA (probe temperature: 30 °C) and 3-nitrobenzyl alcohol as matrix. The IR measurements were carried out for KBr pellets on a SPECORD 75 IR spectrometer, EPR spectra in the X-band (ν = 9.5 GHz) on a Bruker ESP 300E in CH_2Cl_2 (T = 295 K) or MeCN (T = 130 K) solutions. The EPR parameters were obtained by means of the usual second-order expressions.[49] Simulations were carried out using a modified version of the computer program written by White and Belford.[50]

The compounds Na_2mnt,[51] H_2detcb[52] and $[NBu_4][ReOCl_4]$[53] have been prepared by literature procedures; Ph_3P, Me_2PhP and $NaS_2CNEt_2\cdot 3H_2O$ were obtained commercially (Aldrich).

Preparations

$[NBu_4][ReO_4]$. Rhenium powder (1 g) was placed in a flask (200 cm^3) and H_2O_2 (30%, 50 cm^3) and an aqueous NH_3 solution (2 cm^3) were added carefully. The mixture was stirred for 1 h at ambient temperature. Oxidation of the metal was completed by addition of H_2O_2 (50 cm^3) and heating until a clear solution was obtained. It is important to keep the solution basic to avoid the formation of a considerable amount of volatile Re_2O_5 which would lead to a decrease of the yield. When a clear solution was obtained the mixture was boiled to destroy the residual peroxide and an excess of NBu_4Br in water was added. The colourless precipitate was filtered off and recrystallized from methanol. Yield: almost quantitative (Found: C, 38.7; H, 3.4; N, 2.7. $C_{16}H_{36}NO_4Re$ requires C, 38.9; H, 3.2; N, 2.8%). IR: ν(ReO) 913 and 905 cm^{-1}.

$[NBu_4][ReNCl_4]$. *Method* (*a*). The compound $[NBu_4][ReO_4]$ (493 mg, 1 mmol) was dissolved in ethanol (50 cm^3) and a stream of HCl was slowly bubbled through the solution. The temperature was kept at 20 °C to avoid the formation of rhenium(IV) side products. After 10 min NaN_3 (100 mg) in the minimum volume of water was added and the reaction with HCl continued. After 1 h NaN_3 (100 mg) was added. Then the mixture was saturated with HCl and kept in the stoppered flask overnight at ambient temperature. After addition of a third portion (100 mg) of NaN_3 and bubbling HCl gas through the solution the volume was reduced by a stream of nitrogen to about 10 cm^3. Upon cooling to −30 °C greenish yellow plates of $[NBu_4][ReNCl_4]$ deposited which were filtered off and recrystallized from CH_2Cl_2–xylene. More product could be obtained by further evaporation of the mother-liquor. Yellow crystals, yield 70%.

Method (*b*). The compound $[NBu_4][ReO_4]$ (493 mg, 1 mmol) was dissolved in CH_2Cl_2 (50 cm^3). The solution was saturated with HCl gas at a temperature of 20 °C. The compound $SiMe_3N_3$ (100 μl) was added which led to a deep red colour and HCl gas was bubbled through the solution for 10 min. The flask was sealed and upon standing overnight a yellow solution formed which was treated with HCl gas and $SiMe_3N_3$ as described above. The solvent was reduced to about 10 cm^3 and the same volume of diethyl ether added. Bright yellow crystals of $[NBu_4][ReNCl_4]$ deposited on storing at −30 °C. Yield: 45% (Found: C, 32.7; H, 6.4; Cl, 24.3; N, 4.5%. $C_{16}H_{36}Cl_4N_2Re$ requires C, 32.8; H, 6.2; Cl, 24.3; N, 4.8%). IR: ν(ReN) 1103, ν(ReCl) 329 cm^{-1}. FAB mass spectrum: m/z = 341 ($[ReNCl_4]^-$), 306 ($[ReNCl_3]^-$) and 271 ($[ReNCl_2]^-$).

$Cs_2[ReNCl_5]$. A solution of $[NH_4][ReO_4]$ (1 mmol) in ethanol (50 cm^3) was treated with HCl gas and sodium azide as described for the synthesis of $[NBu_4][ReNCl_4]$. After reducing the volume of the final reaction mixture to about 10 cm^3 a solution of CsCl (2 mmol) in ethanol (20 cm^3) was added which resulted in the formation of a yellow solid. The product was filtered off, washed with HCl-saturated ethanol and dried in vacuum. Yellow powder, yield 80% (Found: Cl, 27.8; N, 1.8. Cl_5Cs_2NRe requires Cl, 27.5; N, 2.2%). IR: ν(ReN) 1134, ν(ReCl) 1053, 336 and 318 cm^{-1}.

$[NBu_4][ReNBr_4]$. The compound $[NBu_4][ReNCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetonitrile (*ca.* 10 cm^3) and HBr (48%,

Table 4 Crystal structure data collection and refinement parameters

	$[NBu_4][ReNCl_4]$	$[ReN(Hdetcb)_2]$	$[NBu_4]_2[ReN(mnt)_2]$	$[NBu_4][ReO(mnt)_2]$
Crystal dimensions/mm	0.3 × 0.15 × 0.15	0.3 × 0.2 × 0.15	0.35 × 0.2 × 0.2	0.2 × 0.2 × 0.1
Formula	$C_{16}H_{36}Cl_4N_2Re$	$C_{24}H_{32}N_7ReS_2$	$C_{40}H_{72}N_7ReS_4$	$C_{24}H_{36}N_5OReS_4$
M	584.46	668.89	965.49	752.02
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic
Space group	$P4/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	11.795(1)	9.806(2)	12.658(1)	11.815(3)
b/Å	11.795(1)	11.242(2)	15.608(2)	11.938(3)
c/Å	8.466(1)	12.336(3)	25.934(3)	12.541(3)
α/°		75.34(2)		86.35(2)
β/°		79.34(2)	102.54(1)	86.35(2)
γ/°		87.72(2)		60.64(2)
U/Å^3	1177.8(2)	1294.7(5)	5001.4(9)	1537.4(6)
Z	2	2	4	2
D_c/g cm^{-3}	1.648	1.716	1.282	1.566
Measuring temperature (°C)	20	−50	20	20
Scan type	ω	ω	ω	ω
μ/mm^{-1}	5.613	4.881	6.553	4.248
Absorption correction	DIFABS[56]	Ψ Scans	Ψ Scans	DIFABS[56]
T_{min}, T_{max}	0.260, 1.000	0.9366, 0.9999	0.895, 0.995	0.9251, 0.9972
Weighting scheme $[P = (F_o^2 + 2F_c^2)/3]$, w^{-1}	$\sigma^2(F_o^2) + (0.0413P)^2 + 0.7528P$	$\sigma^2(F_o^2) + (0.0311P)^2 + 1.5938P$	$\sigma^2(F_o^2) + (0.0529P)^2 + 9.6248P$	$\sigma^2(F_o^2) + (0.0215P)^2 + 1.3008P$
Measured reflections	1531	8000	11 001	5688
Independent reflections	1164	6853	8894	5684
$[I > 2\sigma(I)]$	1023	5809	6489	4457
Refined parameters	77	315	455	316
$R1$ (F), $wR2$ (F^2)	0.241, 0.0592	0.0359, 0.0711	0.0493, 0.1156	0.0373, 0.0638
Goodness of fit	1.051	1.112	1.079	1.1457
Programs used	SHELXS 86,[54] SHELXL 93,[55] PLATON,[57] HELENA[57]	SHELXS 86,[54] SHELXL 93,[55] PLATON,[57] HELENA[57]	SHELXS 86,[54] SHELXL 93,[55] PLATON,[57] HELENA[57]	SHELXS 86,[54] SHELXL 93,[55] PLATON,[57] SDP[58]

100 µl) was added. The mixture was stirred for 1 h at room temperature. After addition of xylene (10 cm^3) and slow evaporation of the solvent $[NBu_4][ReNBr_4]$ crystallized as dark red plates. Yield: almost quantitative (Found: C, 25.2; H, 4.5; Br, 42.1; N, 4.1. $C_{16}H_{36}Br_4N_2Re$ requires C, 25.2; H, 4.7; Br, 41.9; N, 3.7%). IR: ν(ReN) 1077 cm^{-1}.

$[ReN(Hdetcb)_2]$. The compound $[NBu_4][ReNCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetone (50 cm^3) and H_2detcb (70 mg, 0.3 mmol) in acetone (10 cm^3) and a drop of Et_3N were added. The mixture was refluxed for 30 min. During this time it changed from yellow *via* purple and green to dark red. The volume was reduced to about 10 cm^3 and diethyl ether (10 cm^3) added. Upon standing in a refrigerator red crystals of $[ReN(Hdetcb)_2]$ deposited which were collected and recrystallized from CH_2Cl_2–*n*-hexane as red blocks, yield 60% (Found: C, 42.9; H, 4.9; N, 14.6; S, 9.1. $C_{24}H_{32}N_7ReS_2$ requires C, 43.0; H, 4.8; N, 14.6; S, 9.6%). IR: ν(ReN) 1061 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38 (s, 1 H, NH), 7.76–7.29 (m, 5 H, Ph), δ 3.94 (m, hindered rotation, 4 H, CH_3) and 1.35 (m, hindered rotation, 6 H, CH_3). Positive-ion FAB mass spectrum: *m*/*z* = 669 (18% B, base peak).

$[ReN(S_2CNEt_2)_2]$. The compound $[NBu_4][ReNCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetone (50 cm^3) and $NaS_2CNEt_2\cdot 3H_2O$ (68 mg, 0.3 mmol) in methanol (20 cm^3) added. The mixture was refluxed for 30 min to give a clear yellow solution. The volume was reduced to about 10 cm^3 and diethyl ether (10 cm^3) added. Upon cooling yellow crystals of $[ReN(S_2CNEt_2)_2]$ deposited which were collected, washed with water and methanol and recrystallized from CH_2Cl_2–Pr^{i}OH as yellow blocks, yield 95%. The analytical and spectroscopic data of the product were identical with previously published ones.[48]

$[NBu_4]_2[ReN(mnt)_2]$. The compound $[NBu_4][ReNCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetone (50 cm^3) and Na_2mnt (55 mg, 0.3 mmol) in methanol (20 cm^3) added. The mixture was refluxed for 30 min to give a clear brown solution, NBu_4Br (32 mg, 0.1 mmol) in methanol (10 cm^3) was added and the volume reduced to about 20 cm^3. Upon cooling a yellow solid deposited which was collected, washed with water and recrystallized from acetone–isopropyl alcohol as yellow needles, yield 45% (Found: C, 49.5; H, 7.4; N, 10.2; S, 13.6. $C_{40}H_{72}N_7ReS_4$ requires C, 49.7; H, 7.5; N, 10.2; S, 13.3%). IR: ν(ReN) 1056, ν(C≡N) 2198 cm^{-1}. Negative-ion FAB mass spectrum: *m*/*z* = 481 (100% B) and 713 (M^+ + NBu_4^+).

$[ReNCl_2(Ph_3P)_2]$. The compound $[NBu_4][ReNCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetone (50 cm^3) and Ph_3P (130 mg, 0.5 mmol) in acetone (20 cm^3) added. The mixture was refluxed for 30 min to give a clear yellow-brown solution. Upon standing $[ReNCl_2(Ph_3P)_2]$ crystallized as tiny yellow-brown plates, yield 90%. The analytical and spectroscopic data of the product were identical with previously published ones.[9]

$[ReNCl_2(Me_2PhP)_3]$. The compound $[NBu_4][ReNCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetone (50 cm^3) and an excess of Me_2PhP in acetone (10 cm^3) added. The mixture was refluxed for 10 min to give a clear yellow solution. The volume was reduced to about 10 cm^3 and the same volume of diethyl ether added. Upon standing in a refrigerator yellow crystals of $[ReNCl_2(Me_2PhP)_3]$ deposited. A second fraction of crystals could be obtained by further evaporation of the solvent, yield 70%. The analytical and spectroscopic data of the product were identical with previously published ones.[9]

$[NBu_4][ReO(mnt)_2]$. The compound $[NBu_4][ReOCl_4]$ (60 mg, 0.1 mmol) was dissolved in acetone (10 cm^3) and Na_2mnt (37 mg, 0.2 mmol) in methanol (10 cm^3) added. The mixture was stirred at ambient temperature for 30 min to give a clear brown solution. The volume was reduced to about 10 cm^3 and diethyl ether (10 cm^3) added. Upon cooling a brown solid deposited which was collected, washed with water and recrystallized from acetone–isopropyl alcohol as red-brown blocks, yield 90%

(Found: C, 39.4; H, 4.6; N, 9.5; S, 17.7. $C_{24}H_{36}N_5OReS_4$ requires C, 39.7; H, 5.0; N, 9.7; S, 17.7%). IR: ν(ReO) 976, ν(C≡N) 2209 cm^{-1}. Negative-ion FAB mass spectrum: $m/z = 483$ (M^+, 100% B).

Crystallography

The intensities for the X-ray determinations were collected on an automated single-crystal diffractometer of the type CAD4 (Enraf-Nonius, Delft) with Mo-Kα radiation ($\lambda = 0.710\,73$ Å). The unit-cell dimensions were determined from the angular settings of 25 high-angle reflections. The structures were solved by Patterson synthesis using SHELXS 86.[54] Subsequent Fourier-difference map analysis yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL 93.[55] For [ReN(Hdetcb)$_2$] the positions of the hydrogen atoms were derived from the final Fourier map and have been fully refined. For the other structures H atoms were included at calculated positions and treated using the 'riding model' option of SHELXL 93. In the structure refinement of [NBu_4][$ReNCl_4$] a weak disorder of the metal atom of about 10% has been considered. The disorder has no consequences for the discussion of the structure. Crystal data and more details of the data collections and refinements are contained in Table 4.

CCDC reference number 186/785.

Acknowledgements

We thank the Herrmann Starck AG (Berlin) for generously providing rhenium metal and acknowledge grants from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. U. A. thanks Professor J. Strähle (Tübingen) for his kind hospitality.

References

1 W. Liese, K. Dehnicke, I. Walker and J. Strähle, *Z. Naturforsch.*, *Teil. B*, 1978, **34**, 693.
2 W. Liese, K. Dehnicke, R. D. Rogers, R. Shakir and J. L. Atwood, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 1061.
3 W. Kafitz, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1982, **490**, 175.
4 M. A. A. de C. T. Carrondo, R. Shakir and A. C. Skapski, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 841.
5 K. Dehnicke, W. Liese and P. Köhler, *Z. Naturforsch.*, *Teil B*, 1977, **32**, 1487.
6 H. G. Hauck, P. Klingelhöfer, U. Kynast and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1984, **520**, 18.
7 U. Müller, W. Kafitz and K. Dehnicke, *Naturwissenschaften*, 1982, **69**, 503.
8 U. Müller, W. Kafitz and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **501**, 69.
9 J. Chatt, C. D. Falk, G. J. Leigh and R. J. Paske, *J. Chem. Soc. A*, 1969, 2288.
10 K. Dehnicke and J. Strähle, *Angew. Chem.*, 1981, **93**, 451 and refs. therein.
11 K. Dehnicke and J. Strähle, *Angew. Chem.*, 1992, 104, 978 and refs. therein.
12 R. Hübener, Ph.D. Thesis, University of Tübingen, 1994.
13 R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 723.
14 U. Abram, E. Schulz Lang, S. Abram, J. Wegmann, J. R. Dilworth, R. Kirmse and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 623.
15 J. Baldas, J. F. Boas, J. Bonnyman and G. A. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 2395.
16 B. Lorenz, K. Schmidt, L. Kaden and M. Wahren, *Isotopenpraxis*, 1986, **22**, 444.
17 U. Abram and R. Wollert, *Radiochim. Acta*, 1993, **63**, 149.
18 U. Abram, K. Köhler, R. Kirmse, N. B. Kalinichenko and I. N. Marov, *Inorg. Chim. Acta*, 1990, **176**, 139.
19 J. Baldas, J. F. Boas, J. Bonnyman, S. F. Colmanet and G. A. Williams, *Inorg. Chim. Acta*, 1991, **179**, 189.
20 J. Baldas, S. F. Colmanet and M. F. Mackay, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1890.
21 J. Baldas and S. F. Colmanet, *Inorg. Chim. Acta*, 1990, **176**, 1.
22 J. Baldas, J. Bonnyman and G. A. Williams, *Inorg. Chem.*, 1986, **25**, 150; J. Baldas, *Adv. Inorg. Chem.*, 1994, **41**, 1 and refs. therein.
23 L. Zsolnai, ZORTEP, a program for ellipsoid presentations of crystal structures, University of Heidelberg, 1994.
24 G. M. Lack and J. F. Gibson, *J. Mol. Struct.*, 1978, **46**, 299.
25 A. Voigt, U. Abram, P. Strauch and R. Kirmse, *Inorg. Chim. Acta*, in the press.
26 R. Kirmse, J. Stach and U. Abram, *Inorg. Chim. Acta*, 1980, **117**, 117.
27 I. N. Marov and N. A. Kostromina, *EPR and NMR in the Chemistry of Coordination Compounds*, Nauka, Moscow, 1979 (in Russian).
28 K. Dehnicke, H. Prinz, W. Kafitz and R. Kujanek, *Liebigs Ann. Chem.*, 1981, 20.
29 B. Lorenz, P. Kränke, K. Schmidt, R. Kirmse, R. Hübener and U. Abram, *Z. Anorg. Allg. Chem.*, 1994, **620**, 921.
30 J. Baldas, J. F. Boas, S. F. Colmanet and G. A. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2441.
31 K. A. Walton, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (Editors), *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1st edn., 1987, vol. 4, p. 125 and refs. therein.
32 U. Abram and S. Ritter, *Inorg. Chim. Acta*, 1993, **210**, 99.
33 S. Ritter, Ph.D. Thesis, University of Tübingen, 1994.
34 U. Abram and S. Ritter, *Inorg. Chim. Acta*, 1994, **216**, 31.
35 U. Abram and R. Hübener, *Inorg. Chim. Acta*, 1993, **206**, 231.
36 U. Abram, R. Münze, J. Hartung, L. Beyer, R. Kirmse, K. Köhler, J. Stach, H. Behm and P. T. Beurskens, *Inorg. Chem.*, 1989, **28**, 834.
37 U. Abram, S. Abram and J. R. Dilworth, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1257.
38 E. Keller, SCHAKAL, a program for presentation of crystal structures, University of Freiburg, 1992.
39 R. Münze, U. Abram, H. Spies and J. Pietzsch, in U. Mazzi, *Technetium and Rhenium in Chemistry and Nuclear Medicine 3*, eds. G. Bandoli and M. Niccolini, Raven Press, New York, and Cortina International, Verona, p. 177.
40 U. Abram, S. Abram, J. Stach, W. Dietzsch and W. Hiller, *Z. Naturforsch.*, *Teil B*, 1991, **46**, 1183.
41 G. Bandoli, U. Mazzi, U. Abram, H. Spies and R. Münze, *Polyhedron*, 1987, **6**, 1547.
42 G. A. Williams and J. Baldas, *Aust. J. Chem.*, 1989, **42**, 875.
43 S. F. Colmanet and M. F. Mackay, *Aust. J. Chem.*, 1988, **41**, 151.
44 S. F. Colmanet and M. F. Mackay, *Inorg. Chim. Acta*, 1988, **147**, 173.
45 J. Baldas, J. Bonnyman and G. A. Williams, *Aust. J. Chem.*, 1985, **38**, 215.
46 R. Hübener and U. Abram, *Z. Anorg. Allg. Chem.*, 1992, **617**, 96.
47 R. Kirmse, K. Köhler, U. Abram, R. Böttcher, L. Golic and E. deBoer, *Chem. Phys.*, 1990, **143**, 75.
48 J. F. Rowbottom and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 826.
49 B. Bleaney, *Philos. Mag.*, 1951, **42**, 441.
50 L. K. White and R. L. Belford, *J. Am. Chem. Soc.*, 1976, **98**, 4428; L. K. White, Ph.D. Dissertation, Urbana, Illinois, 1997, revised version written by K. Köhler and R. Böttcher, University of Leipzig, 1990.
51 G. Bähr and G Schleitzer, *Chem. Ber.*, 1957, **90**, 438.
52 L. Beyer, J. Hartung and R. Widera, *Tetrahedron*, 1984, **40**, 405.
53 R. Alberto, R. Schibli, A. Egli, P. A. Schubiger, W. A. Herrmann, G. Artus, U. Abram and T. A. Kaden, *J. Organomet. Chem.*, 1995, **493**, 119.
54 G. M. Sheldrick, SHELXS 86, a program for the solution of crystal structures, University of Göttingen, 1986.
55 G. M. Sheldrick, SHELXL 93, a program for the refinement of crystal structures, University of Göttingen, 1993.
56 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
57 A. Spek, PLATON and HELENA, programs for data reduction and handling of crystal structure data, University of Utrecht, 1994.
58 B. A. Frenz, SDP, a structure determination package, version 3.0, College Station, TX, and Enraf-Nonius, Delft, 1986.

Received 12*th August* 1997; *Paper* 7/05881K