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Technetium(V) and rhenium(V) nitrido complexes with bis(diphenylthiophosphoryl)amide, $N(SPPh_2)_2^-$ †

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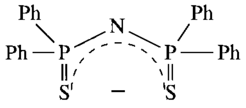
Technetium(V) and rhenium(V) nitrido complexes of the compositions $[MNL_2]$ and $[MN(Cl)(PPhMe_2)L]$ have been synthesized by reaction of $Na[N(SPPh_2)_2]$ and $[MNCl_2(PPh_3)_2]$ or $[MNCl_2(PPhMe_2)_3]$ complexes, respectively [M = Re or Tc; L = $N(SPPh_2)_2^-$]. The amide anion acts in all isolated complexes as a chelating ligand co-ordinated *via* the sulfur atoms. The complexes $[TcN\{N(SPPh_2)_2\}_2]$, $[ReN\{N(SPPh_2)_2\}_2]$ and $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ have been studied by X-ray crystallography. The bis-chelates are five-co-ordinate with the nitrogen atoms at the apexes of square pyramids. The Tc atom in $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ has a distorted-octahedral co-ordination sphere with Cl bonded *trans* to the nitrido function. The complex $[ReN\{N(SPPh_2)_2\}_2]$ is the first five-co-ordinate nitride which reacts with BCl_3 to form a nitrido bridge between rhenium and boron; $[Re(NBCl_3)\{N(SPPh_2)_2\}_2]$ is characterized by a covalent N–B bond of 1.539(5) Å. The Re–N multiple bond distance is only slightly influenced by addition of the Lewis acid. The complex $[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ reacts with BCl_3 with substitution of $N(SPPh_2)_2^-$ and formation of the well known $[Re(NBCl_3)Cl_2(PPhMe_2)_3]$. The corresponding technetium complexes do not form Tc–N–B bridges upon reactions with BCl_3. The $[MN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ (M = Tc or Re) complexes reacted with S_2Cl_2 to give thionitrosyl compounds with the metals in lower oxidation states; $[Re(NS)Cl_2(PPhMe_2)_3]$ and $[Re(NS)Cl_3(PPhMe_2)_2]$ have been characterized spectroscopically, $[Tc(NS)Cl_3(PPhMe_2)_2]$ was studied by X-ray diffraction and EPR spectroscopy. The phosphine ligands are *trans* to each other.

Technetium and rhenium possess radioactive nuclides with potential for nuclear medical applications. The favourable nuclear properties of the metastable isotope ^{99m}Tc (γ-emitter with $E = 140$ keV, half-life $t_{\frac{1}{2}} = 6.02$ h) allow images with high resolution to be obtained with a low radiation dose to the patient and make the element predominant in clinical organ imaging.[1] More than 80% of all diagnostic studies in routine nuclear medicine are presently performed with ^{99m}Tc radiopharmaceuticals.[2] Rhenium-186 is under discussion as one of the most promising radionuclides for application in palliative treatment of cancer and radioimmunotherapy.[3,4] Detailed co-ordination chemical studies are required to estimate the possibilities of the designing of identical radiopharmaceutical kits for both diagnosis and therapy (which is suggested by the relatively similar chemistry of the elements). They should also consider the higher kinetic stability of rhenium complexes over their technetium analogues and differences in the reactivity of ligands. Since technetium does not possess stable isotopes, chemical studies are commonly performed with the long-lived nuclide ^{99}Tc (weak β-emitter, $E_{max} = 0.3$ MeV, $t_{\frac{1}{2}} = 2.12 \times 10^5$ years) which is easily available in macroscopic amounts from fission products and can be handled using conventional laboratory equipment.[5]

Complexes with the amide **I** have been discussed as models for the co-ordination sites of metalloenzymes.[6] Tetrahedral bis-co-ordinated complexes with divalent metal ions have been confirmed for Ni^{II} and Cu^{II} by X-ray crystallography and EPR spectroscopy, respectively.[6,7] Rossi *et al.*[8,9] studied the co-ordination behaviour of $Ph_2P(X)NH(X)PPh_2$ (X = O or S) and $K[Ph_2P(Se)N(Se)PPh_2]$ towards the $[ReO]^{3+}$ core and reported a considerable tendency for the products to decompose with loss of the chalcogen donor atoms. More recently, the same group described some reactions of rhenium(V) imido and nitrido complexes with these compounds and found the nitrogen-containing $[ReN]^{2+}$ and $[ReNMe]^{3+}$ cores more suitable to stabilize complexes with the 'soft' sulfur donor sites of $[(Ph_2PS)_2N]^-$ than the oxorhenium(V) centre.[10] The reported reaction patterns show a strong dependence of the isolated products on the reaction conditions and suggested that further studies with different rhenium starting materials and comparable technetium compounds would be valuable.



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In the present paper we describe the reactivity of $Na[N(SPPh_2)_2]$ with $[MNCl_2(PPh_3)_2]$, $[MNCl_2(PPhMe_2)_3]$ (M = Tc or Re) and $[NBu_4][TcNCl_4]$. The products have been characterized chemically and by X-ray crystallography. Attempted reactions of the nitride ligand show clear differences between analogous rhenium and technetium complexes.

Results and Discussion

The anion $[N(SPPh_2)_2]^-$ acts as bidentate, *S,S′*-co-ordinated ligand in all the rhenium(V) and technetium(V) nitrido complexes

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† *Non-SI units employed:* G = 10^{-4} T, eV ≈ 1.60×10^{-19} J.

Table 1 Selected bond lengths (Å) and angles (°) in $[TcN\{N(SPPh_2)_2\}_2]$ and $[ReN\{N(SPPh_2)_2\}_2]$

$[TcN\{N(SPPh_2)_2\}_2]$		$[ReN\{N(SPPh_2)_2\}_2]$	
Tc–N(10)	1.608(5)	Re–N(10)	1.647(7)
Tc–S(1)	2.448(2)	Re–S(1)	2.393(2)
Tc–S(2)	2.405(2)	Re–S(2)	2.422(2)
Tc–S(3)	2.438(2)	Re–S(3)	2.432(2)
Tc–S(4)	2.451(2)	Re–S(4)	2.412(2)
S(1)–P(1)	2.026(2)	S(1)–P(1)	2.047(3)
S(2)–P(2)	2.041(5)	S(2)–P(2)	2.035(3)
P(1)–N(1)	1.597(5)	P(1)–N(1)	1.579(6)
P(2)–N(1)	1.596(5)	P(2)–N(1)	1.588(6)
S(3)–P(3)	2.031(2)	S(3)–P(3)	2.036(3)
S(4)–P(4)	2.027(2)	S(4)–P(4)	2.038(3)
P(3)–N(2)	1.584(5)	P(3)–N(2)	1.601(1)
P(4)–N(2)	1.600(5)	P(4)–N(2)	1.590(6)
N(10)–Tc–S(1)	103.9(2)	N(10)–Re–S(1)	105.3(2)
N(10)–Tc–S(2)	105.2(2)	N(10)–Re–S(2)	101.9(3)
N(10)–Tc–S(3)	105.8(3)	N(10)–Re–S(3)	100.9(3)
N(10)–Tc–S(4)	102.1(2)	N(10)–Re–S(4)	105.2(2)
S(1)–Tc–S(2)	95.44(6)	S(1)–Re–S(2)	97.18(7)
S(1)–Tc–S(3)	75.71(6)	S(1)–Re–S(3)	77.71(7)
S(1)–Tc–S(4)	154.03(7)	S(1)–Re–S(4)	149.15(8)
S(2)–Tc–S(3)	148.95(7)	S(2)–Re–S(3)	157.18(8)
S(2)–Tc–S(4)	77.73(5)	S(2)–Re–S(4)	76.13(7)
S(3)–Tc–S(4)	97.15(6)	S(3)–Re–S(4)	96.84(7)
S(1)–P(1)–N(1)	117.3(2)	S(1)–P(1)–N(1)	117.3(2)
S(2)–P(2)–N(1)	155.5(2)	S(2)–P(2)–N(1)	117.0(2)
P(1)–N(1)–P(2)	123.7(3)	P(1)–N(1)–P(2)	129.9(4)
S(3)–P(3)–N(2)	117.2(2)	S(3)–P(3)–N(2)	117.3(2)
S(4)–P(4)–N(2)	117.6(2)	S(4)–P(4)–N(2)	117.0(2)
P(3)–N(2)–P(4)	124.8(3)	P(3)–N(2)–P(4)	126.0(4)

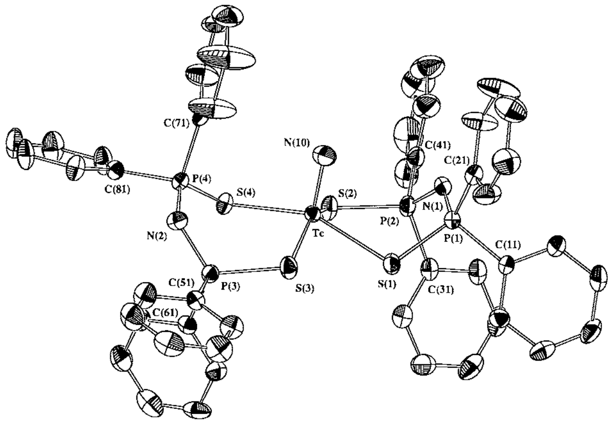

Fig. 1 Molecular structure of $[TcN\{N(SPPh_2)_2\}_2]$ along with the atomic numbering scheme (thermal ellipsoids represent 50% probability)[12]

isolated. No evidence was found for the abstraction of sulfur from the ligand. Its sodium salt, however, seems to be a strong base. Whenever an excess of it was used in protic solvents such as alcohols colourless plates could be isolated as a by-product which were identified as $(Ph_2PS)_2NH$.

Five-co-ordinate bis-chelates of the general formula $[MNL_2]$ are formed when $[MNCl_2(PPh_3)_2]$ (M = Tc or Re) or $[NBu_4][TcNCl_4]$ was used as precursor. In the latter case the metal is rapidly reduced to the oxidation state '+5'. The reductive ligand exchange Cl^- *vs.* $[N(SPPh_2)_2]^-$ proceeds *via* technetium(VI) intermediates. This is evident from the deep blue-green reaction solution. By EPR spectroscopy we identified two additional technetium(VI) complexes in reaction mixtures besides the $[TcNCl_4]^-$ anion, the EPR spectrum of which is well known.[11] The signal intensity of the intermediates, however, rapidly decreases and extensive overlapping in the perpendicular part of the frozen-solution spectra prevent a detailed analysis of the spectral parameters for the individual species. After 2 min at room temperature the reduction of the metal was completed and no more technetium(VI) species could be detected.

During the reactions of $[TcNCl_2(PPh_3)_2]$ and $[ReNCl_2(PPh_3)_2]$ with $Na[N(SPPh_2)_2]$ no intermediates of formula $[MN(Cl)(PPh_3)\{N(SPPh_2)_2\}]$ were detected. This result agrees with the findings in ref. 10 where the formation of $[ReN(Cl)(PPh_3)\{N(SPPh_2)_2\}]$ could only be observed when the less-reactive protonated ligand $(Ph_2PS)_2NH$ was used instead of its lithium salt. The complexes $[TcN\{N(SPPh_2)_2\}_2]$ and $[ReN\{N(SPPh_2)_2\}_2]$ are both air-stable, yellow solids which are soluble in dichloromethane or chloroform. In the IR spectrum (Nujol mulls) of the technetium complex the Tc≡N vibration can be assigned to a band at 1081 cm^{-1}. The corresponding frequency for $[ReN\{N(SPPh_2)_2\}_2]$ (KBr pellets) can be detected at 1085 cm^{-1} as a shoulder to a broad absorption of the ligand at 1107 cm^{-1}. The proton-decoupled ^{31}P NMR spectra of the complexes show sharp singlets at δ 38.8 (Tc) and 39.3 (Re), respectively. The NMR patterns point to the equivalence of the four phosphorus atoms in the ligands and, thus, suggest a square-pyramidal arrangement of the chelating ligands. No significant changes in the ^{31}P chemical shift could be observed as a consequence of the chelate formation $\{Na[N(SPPh_2)_2]$ in methanol: $\delta(^{31}P)$ 39.6}. The positive-ion FAB mass spectra of $[ReN\{N(SPPh_2)_2\}_2]$ show the molecular ion peak at m/z = 1097 with an intensity of 75% B. Only a few fragments can be observed which can be assigned to loss of phenyl groups and/or complete ligands. Ligand decomposition preferentially occurs in the P–S bond.

Single crystals of $[TcN\{N(SPPh_2)_2\}_2]$ and $[ReN\{N(SPPh_2)_2\}_2]$ of X-ray quality were obtained from CH_2Cl_2–methanol solutions. Both compounds crystallize with one molecule solvent CH_2Cl_2, but in different crystal systems. The monoclinic space group $P2_1/c$ was found for $[TcN\{N(SPPh_2)_2\}_2]$, whereas $[ReN\{N(SPPh_2)_2\}_2]$ crystallizes in the triclinic space group $P\bar{1}$. An ORTEP representation[12] of $[TcN\{N(SPPh_2)_2\}_2]$ is given in Fig. 1. No visible differences in the molecular structure of the rhenium analogue are evident. Therefore, the structure plot is omitted for brevity. The labelling scheme of the atoms is the same as for $[TcN\{N(SPPh_2)_2\}_2]$. Selected bond lengths and angles of both bis-chelates are compared in Table 1. The metal atoms in the complexes are displaced by about 0.60 Å from the basal plane of a square pyramid. The metal–nitrogen bonds with Tc–N(10) of 1.608(5) Å and Re–N(10) of 1.647(7) Å can be considered as typical triple bonds and compare with previously reported values.[5,10] For both compounds metal–sulfur bond distances between 2.393(2) and 2.451(2) Å have been found. The P–S distances are lengthened by a mean value of 0.06 Å and the P–N distances shortened by 0.09 Å with regard to the pro-ligand.[13] This relates to delocalization of π-electron density in the chelate rings although the six-membered chelate rings are not planar.

With $[MNCl_2(PPhMe_2)_3]$ (M = Tc or Re) and $Na[N(SPPh_2)_2]$ mixed-ligand complexes of technetium(V) and rhenium(V) can be synthesized with two phosphine ligands in the co-ordination sphere. The complex $[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ is formed at room temperature practically independent of the $[ReNCl_2(PPhMe_2)_3]$: ligand ratio. Upon heating, an increasing amount of the bis-chelate is only formed with a large excess of $Na[N(SPPh_2)_2]$. The more labile $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ can only be obtained when equimolar amounts of the $[N(SPPh_2)_2]^-$ anion are used. The same tendency has been observed in the reaction of $[MNCl_2(PPhMe_2)_3]$ complexes (M = Tc or Re) with thiocarbamoylbenzamidines, which also form six-membered chelate rings.[14,15] Further ligand-exchange reactions could be observed for dithiocarbamates (four-membered ring chelate ligands) where complexes of composition $[MN(PPhMe_2)L_2]$ are formed for both metals.[15,16]

The complexes $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ and $[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ are yellow, air-stable complexes which are readily soluble in dichloromethane or chloroform.

Table 2 Selected bond lengths (Å) and angles (°) in $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$

Tc–N(10)	1.639(3)	Tc–Cl	2.661(1)
Tc–S(1)	2.508(1)	Tc–P(3)	2.441(1)
Tc–S(2)	2.505(1)	Tc–P(4)	2.431(1)
S(1)–P(1)	2.019(1)	S(2)–P(2)	2.012(1)
P(1)–N(1)	1.596(2)	P(2)–N(1)	1.588(2)
N(10)–Tc–S(1)	99.8(1)	N(10)–Tc–S(2)	106.4(1)
N(10)–Tc–P(3)	95.7(1)	N(10)–Tc–P(4)	86.9(1)
N(10)–Tc–Cl	107.8(2)	Tc–S(1)–P(1)	106.34(5)
Tc–S(2)–P(2)	170.49(9)	S(1)–P(1)–N(1)	103.18(4)
S(1)–Tc–S(2)	88.25(3)	P(3)–Tc–P(4)	96.42(4)
S(1)–Tc–P(3)	86.46(4)	S(2)–Tc–P(4)	86.46(4)
S(1)–Tc–P(4)	172.40(3)	S(2)–Tc–P(3)	157.81(3)

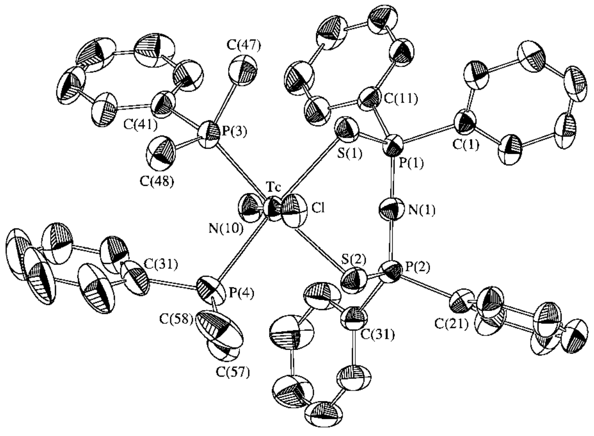

Fig. 2 Molecular structure of $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$. Details as in Fig. 1

The infrared frequencies of the M≡N bonds can be resolved as sharp absorptions at 1060 and 1055 cm^{-1}, respectively. The ^{31}P NMR spectra of the complexes show the signals of the phosphine ligands at about δ −20 and those of the amide at about δ 42. A detailed analysis of the coupling patterns suggests AA′BB′ spin systems with coupling constants of 4 Hz in the AA′ and 6 Hz in the BB′ parts of the spectra. The positive-ion FAB mass spectrometric fragmentation of $[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ shows signals at *m/z* = 924, 822 and 787 which can be assigned to $[ReN(PPhMe_2)_2\{N(SPPh_2)_2\}]^+$, $[ReN(Cl)(PPhMe_2)\{N(SPPh_2)_2\}]^+$ and $[ReN(PPhMe_2)\{N(SPPh_2)_2\}]^+$. No evidence could be found for the molecular ion peak. This is in good agreement with the results of mass spectrometric studies on other six-co-ordinate nitrido complexes of rhenium where generally a preferred cleavage of the bond *trans* to the nitride ligand was observed.[14,16,17]

Crystals of $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ suitable for X-ray crystallography were obtained from an ethanolic solution of the complex. The compound crystallizes in the triclinic space group $P\bar{1}$ together with one molecule of the solvent ethanol. Characteristic bond lengths and angles are given in Table 2. Fig. 2 shows an ellipsoid representation[12] of the complex molecule together with the atomic numbering scheme. The rhenium atom is octahedrally co-ordinated with the Me_2PhP and the chelating ligands in equatorial positions. Distortions from the idealized octahedral geometry are evident. The angle N(10)–Tc–P(4) of 86.9(1)° is much smaller than those to the other equatorially co-ordinated ligands which range between 95.7(1) and 106.4(1)°. The geometry of the molecule is, thus, directly comparable with rhenium complexes of the general composition $[ReN(Cl)(PPhMe_2)_2L]$ where L represents dialkyldithiocarbamate[16] or *N*,*N*′-dialkylthiocarbamoylbenzamidinate.[14] The exceptionally long Tc–Cl bond is due to the *trans* labilizing influence of the multiply bonded nitride ligand. The bonding situation in $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ therefore comes close to that in the analogous rhenium complex $[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$, the crystal structure of which has been published elsewhere.[18]

Table 3 Selected bond lengths (Å) and angles (°) in $[Re(NBCl_3)\{N(SPPh_2)_2\}_2]$

Re–N(10)	1.672(3)	Re–S(1)	2.398(1)
Re–S(2)	2.373(1)	Re–S(3)	2.393(1)
Re–S(4)	2.377(1)	N(10)–B	1.539(5)
B–Cl(1)	1.823(5)	B–Cl(2)	1.850(4)
B–Cl(3)	1.839(5)	S(1)–P(1)	2.057(1)
S(2)–P(2)	2.059(1)	S(3)–P(3)	2.059(1)
S(4)–P(4)	2.057(1)	P(1)–N(1)	1.593(3)
P(2)–N(1)	1.587(3)	P(3)–N(2)	1.583(3)
P(4)–N(2)	1.596(3)		
N(10)–Re–S(1)	106.6(1)	N(10)–Re–S(2)	107.7(1)
N(10)–Re–S(3)	109.5(1)	N(10)–Re–S(4)	104.0(1)
Re–N(10)–B	176.0(3)	N(10)–B–Cl(1)	109.2(3)
N(10)–B–Cl(2)	107.3(3)	N(10)–B–Cl(3)	109.3(3)
S(1)–Re–S(2)	99.03(4)	S(1)–Re–S(3)	74.02(4)
S(1)–Re–S(4)	149.4(4)	S(2)–Re–S(3)	142.60(4)
S(2)–Re–S(4)	73.33(4)	S(3)–Re–S(4)	93.92(4)
S(1)–P(1)–N(1)	115.9(1)	S(2)–P(2)–N(1)	116.6(1)
P(1)–N(1)–P(2)	128.4(2)	S(3)–P(3)–N(2)	116.8(1)
S(4)–P(4)–N(2)	116.2(1)	P(3)–N(2)–P(4)	125.2(2)
Re–S(1)–P(1)	116.03(5)	Re–S(2)–P(2)	118.40(5)
Re–S(3)–P(3)	112.23(5)	Re–S(4)–P(4)	113.44(5)

The terminal nitride ligands in the novel complexes of Re and Tc are sufficiently reactive to undergo interactions with Lewis-acidic compounds. The compositions of the products are dependent on the metal, the equatorial co-ordination sphere of the starting complexes and the nature of the Lewis-acidic compound.

Boron trichloride adducts are formed when the rhenium complexes described above are treated with BCl_3 in CH_2Cl_2 whereas for the corresponding technetium compounds no products with nitrido bridges between the transition metal and boron could be isolated. When the reactions were attempted at room temperature or under slight heating, only the technetium starting materials could be recovered. Longer refluxing periods with an excess of BCl_3 in dichloromethane resulted in decomposition of the technetium(v) nitrido complexes and the final formation of $[TcCl_6]^{2-}$ which could easily be isolated from the reaction mixtures as tetraphenylarsonium or tetraalkylammonium salts. The reaction of BCl_3 with $[ReN\{N(SPPh_2)_2\}_2]$ yielded red crystals of $[Re(NBCl_3)\{N(SPPh_2)_2\}_2]$. This is the first representative of five-co-ordinate complexes with a Cl_3BN^{3-} ligand. In the IR spectrum the ν(Re≡N) frequency at 1160 cm^{-1} is shifted to shorter wavelengths compared with the corresponding value of $[ReN\{N(SPPh_2)_2\}_2]$. This is in accord with the values for other compounds[19–21] containing nitrogen bridges and can be understood as a consequence of vibration couplings in the bridge.

The complex $[Re(NBCl_3)\{N(SPPh_2)_2\}_2]$ is indefinitely stable as a solid. Solutions of the compound slowly decompose with reformation of $[ReN\{N(SPPh_2)_2\}_2]$. Crystals of the boron trichloride adduct of X-ray quality were obtained from the reaction mixture and from CH_2Cl_2 solutions containing small amounts of BCl_3. The compound crystallizes in the triclinic space group $P\bar{1}$. An ORTEP[12] diagram of the complex molecule along with the atomic numbering scheme is given in Fig. 3. Table 3 contains selected bond distances and angles. The Re atom is five-co-ordinated with the nitride ligand at the apex of a square pyramid. The metal atom is situated 0.69 Å above the basal plane (compared with 0.55 Å in $[ReN\{N(SPPh_2)_2\}_2]$). The Re–N bond length is only slightly influenced by the addition of BCl_3 (1.672 *vs.* 1.648 Å in the starting material). The N–B bond is in the normal range of covalent nitrogen–boron single bonds.

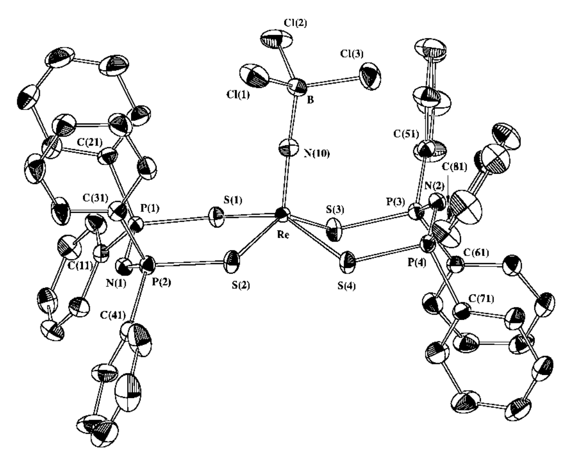

Fig. 3 Molecular structure of [Re(NBCl$_3$){N(SPPh$_2$)$_2$}$_2$]. Details as in Fig. 1

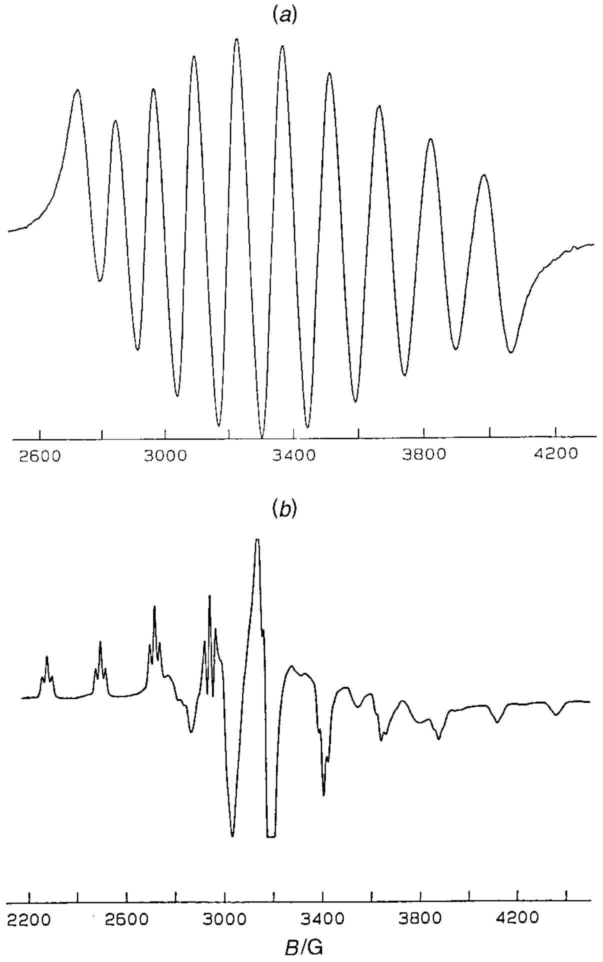

Fig. 4 Experimentally obtained EPR spectra of *trans*-[Tc(NS)Cl$_3$(PPhMe$_2$)$_2$] (CHCl$_3$ solutions) at (*a*) 293 and (*b*) 130 K

No significant changes in the equatorial co-ordination sphere are observed as a consequence of the reaction at the co-ordinated nitride of [ReN{N(SPPh$_2$)$_2$}$_2$]. Despite this result, upon reaction of [ReN(Cl)(PPhMe$_2$)$_2${N(SPPh$_2$)$_2$}] with BCl$_3$ further ligand-exchange reactions have been observed and only the well known [Re(NBCl$_3$)Cl$_3$(PPhMe$_2$)$_2$][22] and small amounts of [Re(NBCl$_3$){N(SPPh$_2$)$_2$}$_2$] could be isolated and spectroscopically characterized.

Reactions of co-ordinated nitride with disulfur dichloride are known to yield thionitrosyl complexes.[23] The complexes [ReN(Cl)(PPhMe$_2$)$_2${N(SPPh$_2$)$_2$}] and [TcN(Cl)(PPhMe$_2$)$_2${N(SPPh$_2$)$_2$}] react with S$_2$Cl$_2$ with complete rearrangement of the co-ordination spheres. The thionitrosyl complexes [Re(NS)Cl$_2$(PPhMe$_2$)$_3$] and [Re(NS)Cl$_3$(PPhMe$_2$)$_2$] with the metal in the formal oxidation states '+1' and '+2' could be isolated from the reaction mixtures. Both NS complexes are formed simultaneously and their ratio depends on the amount of S$_2$Cl$_2$ added. In the corresponding reaction mixtures the formation of the bis-chelates [ReN{N(SPPh$_2$)$_2$}$_2$] as a third product was detected spectroscopically. Recently, we have observed the same reaction pattern with other rhenium(V) mixed-ligand complexes of general formula [ReN(Cl)(PPhMe$_2$)$_2$L] where L$^-$ represents the six-membered chelate ring ligand *N*,*N'*-diethylthiocarbamoylbenzamidinate.[24] In that paper also the molecular structures of *mer*-[Re(NS)Cl$_2$(PPhMe$_2$)$_3$] and *trans*-[Re(NS)Cl$_3$(PPhMe$_2$)$_2$] are discussed in detail. The complex [TcN(Cl)(PPhMe$_2$)$_2${N(SPPh$_2$)$_2$}] reacts with disulfur dichloride in a similar way. Green crystals of *trans*-[Tc(NS)Cl$_3$(PPhMe$_2$)$_2$] are produced with considerable amounts of [TcN{N(SPPh$_2$)$_2$}$_2$]. The formation of *trans*-[Tc(NS)Cl$_3$(PPhMe$_2$)$_2$] is remarkable since recent attempts to prepare this technetium(II) complex always led to red [Tc(NS)Cl$_3$(PPhMe$_2$)(OPPhMe$_2$)] having one phosphine oxide ligand in *trans* position to the thionitrosyl group.[25–27]

The complex [Tc(NS)Cl$_3$(PPhMe$_2$)$_2$] was studied by EPR spectroscopy. With the metal in the formal oxidation state '+2' it has a 4d^5 'low-spin' configuration, $S = \frac{1}{2}$, and gives well resolved EPR spectra even at room temperature. The spectra of liquid solutions [Fig. 4(*a*)] consist of ten hyperfine lines from the interaction of the unpaired electron with the ^{99}Tc nucleus, which possesses a nuclear spin of $I = \frac{9}{2}$. Superhyperfine couplings due to interactions of the unpaired electron with the co-ordinating ^{31}P ($I = \frac{1}{2}$), ^{35,37}Cl ($I = \frac{3}{2}$) or ^{14}N ($I = 1$) nuclei could not be resolved at room temperature. Fig. 4(*b*) shows the EPR spectrum of a frozen CHCl$_3$ solution of *trans*-[Tc(NS)Cl$_3$(PPhMe$_2$)$_2$] at $T = 130$ K. The general feature is characteristic of an axially symmetric, randomly oriented $S = \frac{1}{2}$ system with parallel and perpendicular sets of technetium-99 hyperfine lines as can be described by the Spin Hamiltonian (1)

$$\hat{H}_{sp} = \beta_e[g_{\parallel}B_z\hat{S}_z + g_{\perp}(B_x\hat{S}_x + B_y\hat{S}_y)] + A_{\parallel}^{Tc}\hat{S}_z\hat{I}_z + A_{\perp}^{Tc}(\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y) \quad (1)$$

where $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}^{Tc}$ and $A_{\perp}^{Tc}$ are the principal values of the g and the ^{99}Tc hyperfine tensor A^{Tc}. The spectral parameters are summarized in Table 4 and compared with those of the nitrosyl analogue and the previously reported phosphine/phosphine oxide mixed-ligand complex [Tc(NS)Cl$_3$(PPhMe$_2$)(OPPhMe$_2$)].[27] The Me$_2$PhPO ligand in the latter complex is co-ordinated *trans* to the thionitrosyl group and, thus, only a doublet splitting of the technetium-99 hyperfine structure lines is observed. The frozen-solution EPR spectrum of *trans*-[Tc(NS)Cl$_3$(PPhMe$_2$)$_2$], however, shows a well resolved triplet splitting due to the interaction of the unpaired electron with two equatorially co-ordinated ^{31}P nuclei [Fig. 4(*b*)].

The evidence of resolved ligand hyperfine interactions due to ^{31}P indicates a marked delocalization of spin density into ligand orbitals. Thus, a consideration of the bonding situation in the complex in terms of molecular orbitals (MOs) seems to be reasonable. The experimentally derived EPR spectra suggest an 'in-plane π type' for the MO of the unpaired electron which can be described by expression (2), where $\beta_2{}^2$ and $\beta_2'^2$ are measures

$$\Psi_{MO}(B_2) = \beta_2|d_{xy}> - \beta_2'|\Phi_L> \quad (2)$$

of the covalency of the equatorial metal–ligand bonds in this MO and $|\Phi_L>$ describes the linear combination of mainly p orbitals of the four equatorial ligands. This consideration is in accordance with the results obtained earlier for nitrosyl and thionitrosyl complexes of technetium(II).[28–30] Following the mechanism of McGarvey,[31] the β^2 bonding parameter can be derived from the technetium-99 coupling parameters. The

Table 4 Experimentally derived EPR parameters for *trans*-[Tc(NS)-$Cl_3(PPhMe_2)_2$] and related complexes (coupling constants in 10^{-4} cm^{-1})

	[Tc(NS)Cl_3-($PPhMe_2)_2$]	[Tc(NS)$Cl_3(PPhMe_2)$-($OPPhMe_2$)][26]	[Tc(NO)Cl_3-$(PPhMe_2)_2$][27]
g_0	2.045 ± 0.002	2.032	2.045
$a_0{}^{Tc}$	133.0 ± 2.0	148.6	124.9
$g_\parallel$	2.027 ± 0.002	2.027	2.034
$g_\perp$	2.038 ± 0.003	2.039	2.053
$g_{av}{}^a$	2.034		2.047
$A_\parallel{}^{Tc}$	219.0 ± 2.0	236.7	214.5
$A_\perp{}^{Tc}$	101.6 ± 3.0	106.3	88.0
$A_{av}{}^{Tc\,b}$	148.7	148.6	124.9
$A_\parallel{}^{P}$	19.1 ± 0.3^c	23.7^d	19.1^c
β^2	0.75	0.77	0.75

[a] $g_{av} = (g_\parallel + 2g_\perp)/3$. [b] $g_{av} = (A_\parallel{}^{Tc} + 2A_\perp{}^{Tc})/3$. [c] Triplet. [d] Doublet.

Table 5 Selected bond lengths (Å) and angles (°) in *trans*-[Tc(NS)-$Cl_3(PPhMe_2)_2$]

Tc–N	1.761(4)	Tc–Cl(1)	2.432(1)
Tc–Cl(2)	2.347(1)	Tc–Cl(3)	2.355(1)
Tc–P(1)	2.493(1)	Tc–P(2)	2.482(1)
N–S	1.523(4)		
N–Tc–Cl(1)	177.1(1)	N–Tc–Cl(2)	89.7(1)
N–Tc–Cl(3)	93.8(1)	N–Tc–P(2)	92.1(1)
N–Tc–P(2)	92.1(1)	Cl(1)–Tc–Cl(2)	87.47(5)
Cl(1)–Tc–Cl(3)	89.05(5)	Cl(1)–Tc–P(1)	85.97(5)
Cl(1)–Tc–P(2)	87.39(4)	Cl(2)–Tc–Cl(3)	176.47(5)
Cl(2)–Tc–P(1)	92.05(5)	Cl(2)–Tc–P(2)	92.90(5)
Cl(3)–Tc–P(1)	87.09(5)	Cl(3)–Tc–P(2)	87.55(5)
P(1)–Tc–P(2)	171.53(4)	Tc–N–S	176.2(3)

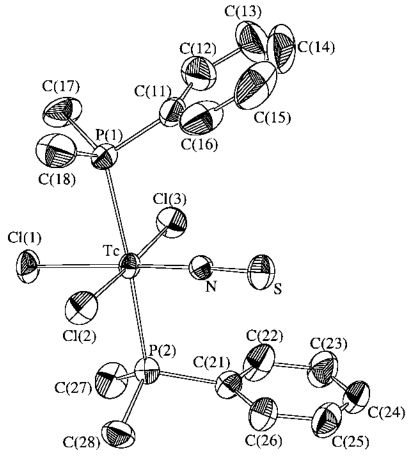

Fig. 5 Molecular structure of *trans*-[Tc(NS)$Cl_3(PPhMe_2)_2$]. Details as in Fig. 1

results for the complexes under discussion are also contained in Table 4. Details of the determination of β^2 have been published previously.[28,30] The somewhat higher covalency in the equatorial co-ordination sphere of *trans*-[Tc(NS)$Cl_3(PPhMe_2)_2$] compared with the situation in [Tc(NS)$Cl_3(PPhMe_2)(OPPhMe_2)$] and the observed similarity with the corresponding nitrosyl complex may be understood in the presence of two π-accepting phosphine ligands.

The results of the EPR spectroscopic study were confirmed by a crystal structure determination on *trans*-[Tc(NS)Cl_3-$(PPhMe_2)_2$]. The complex crystallizes in the triclinic space group *P*1. Suitable crystals were obtained from $CHCl_3$–n-hexane solutions. A representation[12] of the molecular structure along with the numbering scheme is given in Fig. 5. Table 5 contains selected bond lengths and angles. The technetium atom has an only slightly distorted-octahedral environment with the phosphine ligands *trans* to each other. The Tc–N bond distance of 1.761(4) Å is markedly longer than those to terminal nitride ligands or nitrido bridges between a transition metal and a Lewis-acidic compound (*cf.* 1.67 Å in [Re-$(NBCl_3)\{N(SPPh_2)_2\}_2$] or previously published results[19–22]). However, only a weak structural *trans* influence is observed in the thionitrosyl compound compared with the situation in six-co-ordinate nitrido complexes.[16] The resulting TcNS core is nearly linear with a bond angle of 176.2(3)° and, thus, the bonding mode of the thionitrosyl group has to be regarded as NS^+ with extensive back bonding to the Tc^{II}. This is also confirmed by the spectroscopic results discussed above.

Conclusion

The ion $N(SPPh_2)_2{}^-$ is a suitable ligand to stabilize technetium(v) and rhenium(v) nitrido cores. Depending on the reaction conditions and the starting materials used, five- or six-co-ordinate complexes are formed with six-membered chelate rings. Reactions with BCl_3 give nitrido-bridged complexes only with rhenium. For six-co-ordinate complexes of the type [MN(Cl)$(PPhMe_2)_2\{N(SPPh_2)_2\}$] (M = Tc or Re) there is a strong tendency to undergo further ligand exchanges in equatorial positions upon reactions with Lewis acids or S_2Cl_2. Further studies with this ligand system and other technetium and rhenium starting materials are in progress.

Experimental

The complexes [ReN$Cl_2(PPhMe_2)_3$],[31] [ReN$Cl_2(PPh_3)_2$],[32] [TcN-$Cl_2(PPhMe_2)_3$],[33] [TcN$Cl_2(PPh_3)_2$][34] and [NBu_4][TcNCl_4][11] were prepared by previously reported procedures; $(Ph_2PS)_2NH$ was prepared from PPh_2Cl, $NH(SiMe_3)_2$ and sulfur as outlined in ref. 35 and converted *in situ* into the sodium salt by reaction with NaOMe.

The NMR spectra were recorded in $CDCl_3$ solutions on an EX-270 JEOL spectrometer with $SiMe_4$ and H_3PO_4 as internal standards, FAB mass spectra on a MAT 701A spectrometer (Finnigan). Xenon was used as primary beam gas for the latter. The ion gun was operated at 8 kV and 100 μA (probe temperature 30 °C). 3-Nitrobenzyl alcohol was used as matrix. The IR spectra were recorded for KBr pellets (rhenium compounds) or as Nujol mulls (technetium complexes) on a Perkin-Elmer 1330 spectrometer, EPR spectra in $CHCl_3$ solutions on a Bruker ESP-300 spectrometer.

All experiments with the long-lived technetium isotope ^{99}Tc were performed in laboratories approved for the use of long-lived β-emitting radionuclides and appropriate handling techniques were used.

Preparations

[ReN{N(SPPh$_2$)$_2$}$_2$]. The complex [ReN$Cl_2(PPh_3)_2$] (80 mg, 0.1 mmol) was suspended in CH_2Cl_2 (30 cm^3) and Na-[$N(SPPh_2)_2$] (140 mg, 0.3 mmol) was added in MeOH (20 cm^3). The mixture was heated under reflux for about 30 min to give a clear yellow solution. After reducing the volume to about 20 cm^3 a yellow precipitate was formed. Crystallization was completed by standing ovenight in a refrigerator. Recrystallization from CH_2Cl_2–EtOH resulted in yellow blocks, yield 85% (Found: C, 49.5; H, 3.4; N, 3.7; S, 11.0. $C_{49}H_{42}Cl_2N_3P_4ReS_4$ requires C, 49.7; H, 3.6; N, 3.6; S, 10.8%). IR: ν(P_2N) 1196s, 559m; ν(ReN) 1085 cm^{-1}. ^{31}P-{^1H} NMR ($CDCl_3$): δ 39.3 (s). Positive-ion FAB mass spectrum: *m/z* 1097, [ReN-$\{N(SPPh_2)_2\}_2]^+$, 75% B (where B is the base peak); 681, [ReNS-$\{N(SPPh_2)_2\}]^+$, 55% B.

[TcN{N(SPPh$_2$)$_2$}$_2$]. The technetium chelate was prepared following the procedure given above for the rhenium analogue from [TcN$Cl_2(PPh_3)_2$] and Na[$N(SPPh_2)_2$]. Recrystallization from CH_2Cl_2–propan-2-ol, yellow blocks, yield 75%. IR: ν(P_2N)

Table 6 Crystal structure data collection and refinement parameters

	[TcN{N(SPPh$_2$)$_2$}$_2$]·CH$_2$Cl$_2$	[ReN{N(SPPh$_2$)$_2$}$_2$]·CH$_2$Cl$_2$	[TcN(Cl)(PPhMe$_2$)$_2${N(SPPh$_2$)$_2$}]·EtOH	[Re(NBCl$_3$){N(SPPh$_2$)$_2$}$_2$]	[Tc(NS)Cl$_3$(PPhMe$_2$)$_2$]
Crystal dimensions/mm	0.2 × 0.2 × 0.15	0.2 × 0.2 × 0.05	0.4 × 0.2 × 0.15	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.15
Formula	$C_{49}H_{42}Cl_2N_3P_4S_4Tc$	$C_{49}H_{42}Cl_2P_4ReS_4$	$C_{42}H_{48}ClN_2OP_4S_2Tc$	$C_{48}H_{40}BCl_3N_3P_4ReS_4$	$C_{16}H_{22}Cl_3NP_2STc$
M	1093.88	1183.08	918.27	1214.31	526.70
Crystal system	Monoclinic	Triclinic	Triclinic	Tricinlic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	18.078(4)	11.359(5)	10.453(3)	13.104(4)	8.682(2)
b/Å	21.250(3)	14.391(7)	11.790(5)	13.774(5)	8.896(2)
c/Å	13.168(6)	16.761(9)	18.919(6)	14.542(4)	15.096(3)
α/°		110.18(3)	90.54(2)	86.28(2)	97.78(1)
β/°	103.16(4)	89.93(3)	92.52(2)	73.58(2)	93.04(1)
γ/°		93.12(3)	110.43(2)	87.76(2)	106.41(1)
U/Å^3	4926(3)	2567(2)	2182(1)	2511(1)	1103.1(4)
Z	4	2	2	2	2
D_c/g cm^3	1.475	1.529	1.398	1.606	1.586
Radiation (λ/Å)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)	Cu-Kα (1.541 84)
Scan type	ω	ω	ω–2θ	ω	ω
μ/mm^{-1}	0.738	2.794	0.668	2.910	10.892
Absorption correction	None	ψ Scans	None	ψ Scans	ψ Scans
T_{min}, T_{max}		0.976, 0.9903		0.648, 0.999	0.8464, 0.9998
Weighting scheme [$P = (F_o^2 + 2F_c^2)/3$], w^{-1}	$\sigma^2(F_o^2) + (0.0306P)^2 + 7.4613P$	$\sigma^2(F_o^2) + (0.0523P)^2 + 12.3031P$	$\sigma^2(F_o^2) + (0.0577P)^2 + 1.2217P$	$\sigma^2(F_o^2) + (0.0339P)^2 + 0.9622P$	$\sigma^2(F_o^2) + (0.0633P)^2 + 1.8348P$
Measured reflections	9735	12 856	11 096	12 338	4512
Independent reflections	8343	11 139	9511	10 888	3759
Independent reflections [$I > 2\sigma(I)$]	4647	8677	7765	9176	3267
Refined parameters	586	597	488	577	217
$R1$ (F), $wR2$ (F^2)	0.0537, 0.0923	0.0544, 0.1268	0.0392, 0.1015	0.0297, 0.0644	0.0432, 0.1092
Goodness of fit	1.007	1.151	1.081	1.037	1.076
Programs used	SHELXS 86,[36] SHELXL 93,[37] PLATON, HELENA[38]	SHELXS 86,[36] SHELXL 93,[37] PLATON, HELENA[38]	SHELXS 86,[36] SHELXL 93,[37] PLATON, HELENA[38]	SHELXS 86,[36] SHELXL 93,[37] PLATON, HELENA[38]	SHELXS 86,[36] SHELXL 93,[37] PLATON, HELENA[38]

1171s, 561m; ν(TcN) 1081 cm^{-1}. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 38.8 (s).

$[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$. The complex $[ReNCl_2(PPhMe_2)_3]$ (69 mg, 0.1 mmol) was dissolved in MeOH (*ca.* 50 cm^3) and $Na[N(SPPh_2)_2]$ (140 mg, 0.3 mmol) added. The mixture was heated under reflux for about 1 h and reduced in volume to about 20 cm^3. Upon slow cooling a yellow precipitate was formed which was filtered off and recrystallized from CH_2Cl_2–propan-2-ol, yield 70% (Found: C, 49.5; H, 4.5; N, 3.2; S, 6.5. $C_{40}H_{43}ClN_2P_4ReS_2$ requires C, 49.9; H, 4.5; N, 2.9; S, 6.7%). IR: ν(P_2N) 1216s, 570m; ν(ReN) 1055 cm^{-1}. ^{31}P-{^{1}H} NMR ($CDCl_3$): AA′BB′ spin system, δ 42.17, −20.70 (AA′ part, $N = 6$; BB′ part, $N = 4$ Hz). Positive-ion FAB mass spectrum: *m/z* 924, $[ReN(PPhMe_2)_2\{N(SPPh_2)_2\}]^+$, 40% B; 822, $[ReN(Cl)(PPhMe_2)\{N(SPPh_2)_2\}]^+$, 25% B; 787, $[ReN(PPhMe_2)\{N(SPPh_2)_2\}]^+$, 100% B.

$[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$. The complex $[TcNCl_2(PPhMe_2)_3]$ (60 mg, 0.1 mmol) was dissolved in MeOH (*ca.* 50 cm^3) and $Na[N(SPPh_2)_2]$ (94 mg, 0.2 mmol) added. The mixture was heated under reflux for 30 min and reduced in volume to about 20 cm^3. Upon slow cooling a yellow precipitate was formed which was filtered off and recrystallized from CH_2Cl_2–EtOH, yield 70%. IR: ν(P_2N) 1173s, 571m; ν(TcN) 1060 cm^{-1}. ^{31}P-{^{1}H} NMR ($CDCl_3$): AA′BB′ spin system, δ 42.16, −20.70 (AA′ part, $N = 4$; BB′ part, $N = 6$ Hz).

$[Re(NBCl_3)\{N(SPPh_2)_2\}_2]$. The complex $[ReN\{N(SPPh_2)_2\}_2]$ (110 mg, 0.1 mmol) was dissolved in dry CH_2Cl_2 (*ca.* 10 cm^3) and mixed with a 1 mol dm^{-3} solution (1 cm^3) of BCl_3 in CH_2Cl_2. The mixture was stirred at room temperature for 1 h. During this time it changed from yellow to red. The resulting solution was overlayered with hexane (*ca.* 50 cm^3). Upon slow diffusion red crystals were formed which were collected and rinsed with hexane, yield 70% (Found: C, 47.5; H, 3.3; Cl, 8.3; N, 3.5; S, 10.2. $C_{48}H_{40}BCl_3N_3P_4ReS_4$ requires C, 47.4; H, 3.3; Cl, 8.6; N, 3.5; S, 10.5%). IR: ν(P_2N) 1173s, 543m; ν(ReN) 1160 (sh) cm^{-1}. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 35.6 (s). Positive-ion FAB mass spectrum: *m/z* 1179, $[Re(NBCl_2)\{N(SPPh_2)_2\}_2]^+$, 15% B; 1097, $[ReN\{N(SPPh_2)_2\}_2]^+$, 50% B; 1020, $[ReN\{N(SPPh_2)_2\}_2 - Ph]^+$, 10% B; 681, $[ReNS\{N(SPPh_2)_2\}]^+$, 65% B.

***mer*-$[Re(NS)Cl_2(PPhMe_2)_3]$ and *trans*-$[Re(NS)Cl_3(PPhMe_2)_2]$.** The complex $[ReN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ (1.0 mmol) was dissolved in CH_2Cl_2 (*ca.* 100 cm^3) and S_2Cl_2 (140 mg) in CH_2Cl_2 (10 cm^3) was added. After stirring at room temperature for 1 h the volume of the solution was reduced to 10 cm^3 and hexane (50 cm^3) was added. The resulting precipitate was washed with an excess of hexane and redissolved in CH_2Cl_2 (50 cm^3). Addition of hexane (50 cm^3) and standing overnight in a sealed vessel resulted in the formation of red crystals of *mer*-$[Re(NS)Cl_2(PPhMe_2)_3]$. After removal of the stopper and slow evaporation of the solvents blue crystals of *trans*-$[Re(NS)Cl_3(PPhMe_2)_2]$ deposited. Yields: *mer*-$[Re(NS)Cl_2(PPhMe_2)_3]$, 360 mg (45%); *trans*-$[Re(NS)Cl_3(PPhMe_2)_2]$, 95 mg (17%). The spectral data for the complexes are consistent with those previously published.[23]

***trans*-$[Tc(NS)Cl_3(PPhMe_2)_2]$.** The complex $[TcN(Cl)(PPhMe_2)_2\{N(SPPh_2)_2\}]$ (0.1 mmol, 87 mg) was dissolved in CH_2Cl_2 (*ca.* 10 cm^3) and S_2Cl_2 (14 mg) in CH_2Cl_2 (*ca.* 1 cm^3) was added. The mixture was stirred at room temperature for 1 h. Addition of an excess of hexane yielded a dark oil which was redissolved in CH_2Cl_2 (3 cm^3). The resulting solution was overlayered with hexane. After a few days green crystals could be isolated, yield 13 mg (27%). IR: ν(NS) 1220 cm^{-1}.

Crystallography

The intensities for the X-ray determinations were collected at −70 °C on automated single-crystal diffractometers of the type CAD4 (Enraf-Nonius, Delft) using Mo-Kα or Cu-Kα radiation. 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.[36] Subsequent Fourier-difference map analysis yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL 93.[37] The hydrogen atoms were included at calculated positions and regarded using the ‘riding model’ option of SHELXL 93. In the structure refinements of $[TcN\{N(SPPh_2)_2\}_2]\cdot CH_2Cl_2$ and $[ReN\{N(SPPh_2)_2\}_2]\cdot CH_2Cl_2$ weak ‘disorders’ of the metal atoms of about 10% have been considered in the structure calculation. This is often found for five-co-ordinate complexes and is obviously caused by packing effects. No significant changes can be derived for the co-ordination geometry or the ligand binding from this result. The positions are mentioned as footnotes in the corresponding tables. Crystal data and more details of the data collections and refinements are contained in Table 6.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/327.

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