Synthesis and Structure of Bis(diethyldithiocarbamato)nitridotechnetium(V): A Technetium–Nitrogen Triple Bond

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The title compound $[Tc(S_2CNEt_2)_2N]$ has been prepared by the reduction of $[NH_4][TcO_4]$ with hydrazine followed by reaction with $Na[S_2CNEt_2]$. The crystal structure of $[Tc(S_2CNEt_2)_2N]$ has been determined by single-crystal *X*-ray diffraction methods at 17 °C. Crystals are monoclinic, space group $P2_1/c$, with a = 14.823(1), b = 9.159(1), c = 12.865(1) Å, β = 107.98(1)°, and Z = 4. Diffractometry has provided significant Bragg intensities for 2 152 independent reflections and the structure has been refined by full-matrix least-squares methods to R 0.042. The compound, which is isostructural with the rhenium analogue, consists of discrete $[Tc(S_2CNEt_2)_2N]$ molecules, each containing a terminal N^{3-} group. The technetium atom has a distorted square-pyramidal environment with the nitrogen atom in the apical position and four sulphur atoms forming the base. The Tc≡N bond, which has not been observed before, has a length of 1.604(6) Å, and the Tc–S bond distances range between 2.392(2) and 2.405(2) Å.

THE ideal physical properties of technetium-99m ($t_{\frac{1}{2}}$ 6 h, gamma energy 140 keV †) have made this radionuclide the most widely used in diagnostic nuclear medicine.[1] The preparation of technetium-99m complexes for use as organ-imaging agents requires the reduction of the pertechnetate anion prior to chelation. Tin(II) chloride is the most widely used reducing agent for radiopharmaceutical preparation,[1] but formamidinesulphinic acid (aminoiminomethanesulphinic acid) [2] and electrolytic methods [3] have also been used.

The chemistry of technetium-99m in radiopharmaceuticals is poorly understood due to the very low molar concentrations (typically *ca.* 10^{-8} mol dm^{-3}) of the isotope. However, by use of the long-lived technetium-99 nuclide ($t_{\frac{1}{2}}$ 2.12 × 10^5 years), it is possible to isolate technetium compounds which can be characterised by conventional chemical and spectroscopic techniques.

Recently we described the preparation and biological properties of a (dithiocarbamato)technetium-99m complex.[4] This preparation utilised formamidinesulphinic acid as the reducing agent. In the present paper we report the isolation, characterisation, and *X*-ray crystal-structure determination of bis(diethyldithiocarbamato)-nitridotechnetium(V) which results from the reduction of ammonium pertechnetate (^{99}Tc) with hydrazine followed by reaction with sodium diethyldithiocarbamate. This is the first report of a Tc≡N bond.

EXPERIMENTAL

Ammonium [^{99}Tc]pertechnetate and sodium diethyldi-[^{35}S]thiocarbamate were supplied by The Radiochemical Centre, Amersham. Their specific activities were checked by u.v. spectrophotometry and by liquid scintillation counting. Sodium [^{99m}Tc]pertechnetate (70 MBq, supplied by the Australian Atomic Energy Commission) was added in all cases to determine the yield of the technetium-99 compound. The basic alumina used for column chromatography was supplied by B.D.H., Poole, and was activated by heating at 100 °C for 1 h. Chloroform was washed with water, dried, and distilled prior to use.

The i.r. spectrum was determined in a KBr disc on a Perkin-Elmer 197 spectrophotometer and the u.v. spectra were determined on a Beckman Acta CII spectrophotometer. Liquid scintillation counting was performed by use of a Searle Analytic 92 System. Gamma activity was measured either in a Capintec CRC-2N ionisation chamber or in a Packard 5912 Auto-Gamma scintillation spectrometer.

Hydrazine hydrate (0.1 cm^3, 100 mg) was added to a solution of ammonium pertechnetate (3.8 mg) in 5 mol dm^{-3} hydrochloric acid (2 cm^3). The resulting solution was allowed to stand for 10 min. The pH of the solution was then adjusted to 7.0 with 5 mol dm^{-3} sodium hydroxide and a solution of sodium diethyldithiocarbamate (10 mg) in water (1 cm^3) was added. The mixture, which contained a yellow precipitate, was extracted with chloroform (2 × 3 cm^3). The extract was dried over calcium chloride and applied to an alumina column (1 cm diameter × 5 cm). Elution with chloroform gave a yellow fraction which, upon slow evaporation, deposited yellow crystals of bis(diethyldithiocarbamato)nitridotechnetium-99(V); yield 85% based on $[NH_4][TcO_4]$, m.p. 253—254 °C (with decomposition; charring commenced at *ca.* 240 °C) (Found: C, 29.6; H, 5.1; N, 10.1. $C_{10}H_{20}N_3S_4Tc$ requires C, 29.3; H, 4.9; N, 10.3%). The i.r. spectrum showed intense peaks at 1 512, 1 282, 1 204, and 1 070 cm^{-1}.

The diethyldithiocarbamate : technetium ratio was determined in a repeated preparation of the compound in which sodium diethyldi[^{35}S]thiocarbamate and ammonium [^{99}Tc]-pertechnetate containing a tracer amount of [^{99m}Tc]pertechnetate (specific activity 6.7 TBq mmol^{-1} Tc) were used. The ^{99}Tc content in the purified complex was calculated from the ^{99m}Tc gamma count rate (corrected for ^{99m}Tc decay). After the ^{99m}Tc activity was allowed to completely decay (1 week), the ^{35}S activity was determined by difference from the total beta count rate. By use of the measured specific activity of the sodium diethyldi[^{35}S]thiocarbamate (110 kBq mmol^{-1}) the S_2CNEt_2 : Tc ratio was calculated as 2.0 ± 0.1 : 1.

Crystallography.—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of a chloroform–methanol solution of the compound at room temperature. Oscillation and Weissenberg photographs showed the crystals to be monoclinic, and the space group was determined as $P2_1/c$ from the systematic absences. Unit-cell parameters, together with their estimated standard

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† 1 eV ≈ 1.60 × 10^{-19} J.

deviations (e.s.d.s), were derived by a least-squares fit of the 2θ values, for 25 reflections well separated in angle, measured on a diffractometer at 17 °C with Cu-K_α radiation (λ = 1.541 8 Å).

Crystal data. $C_{10}H_{20}N_3S_4Tc$, M = 409.43, Monoclinic, a = 14.823(1), b = 9.159(1), c = 12.865(1) Å, β = 107.98(1)°, U = 1 661.3 Å^3, Z = 4, $F(000)$ = 832, D_c = 1.64 Mg m^{-3}, θ_c = 17 °C, space group $P2_1/c$, μ(Cu-K_α) = 11.24 mm^{-1}.[5]

Intensity data were recorded at 17 °C on a Rigaku–AFC four-circle diffractometer with graphite-monochromatised Cu-K_α radiation. The crystal had well developed (100), (010), and (001) faces with perpendicular distances between parallel faces of 0.16, 0.39, and 0.23 mm respectively. The crystal was sealed in a thin-walled Lindemann glass tube and aligned with the c axis approximately parallel to the diffractometer Φ axis. Intensities were measured by an ω—2θ scan, with a scan rate of 2° min^{-1}, a scan range of $1.2 + 0.5\tan\theta$, and 10-s stationary background counts. Three reference reflections, monitored every 50 reflections, showed no significant variations in intensities during data collection. A total of 2 564 reflections, having non-zero intensities, were measured within the limit $(\sin\theta)/\lambda \leqslant 0.588$ Å^{-1}. Of these, 2 439 were unique and 2 158 were considered observed $[I > 3\sigma(I)]$ and were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarisation effects, and for absorption.[5]

Structure determination and refinement. The structure was solved by the heavy-atom method. The position of the Tc atom was derived from a three-dimensional Patterson map, and subsequent difference-Fourier syntheses revealed the positions of all 18 non-hydrogen atoms. Full-matrix least-squares refinement, with data uncorrected for absorption and with anisotropic temperature factors assigned to all atoms, converged with a reliability index R, defined as $\Sigma\Delta F/\Sigma|F_o|$ where $\Delta F = ||F_o| - |F_c||$, of 0.074. The function minimised was $\Sigma w(\Delta F)^2$, where w is the weight assigned to the $|F_o|$ values. After absorption corrections were applied to the intensity data,[5] with transmission factors ranging between 0.03 and 0.30, the same refinement converged with R 0.051.

Difference syntheses yielded the sites of all hydrogen atoms, and these were included in the scattering model and refined with variable isotropic thermal parameters. An examination of $|F_o|$ and $|F_c|$ values at this stage indicated that a small extinction effect was apparent in the very intense data. Consequently, six intense low-angle reflections were omitted from the refinement. Least-squares refinement {243 variables, 2 152 observations, $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$} converged with R 0.042 and R' $\{= [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ 0.053. The maximum parameter shift-to-error ratios at convergence were 0.2 : 1 for the non-hydrogen atoms [Y/b and Z/c co-ordinates of C(3)], and 0.6 : 1 for the hydrogen atoms [Z/c co-ordinate of H(3B)]. The average parameter shift-to-error ratio for all variables was 0.03 : 1. The largest peaks on a final difference synthesis were of heights 0.59 and −1.15 e Å^{-3} close to the Tc atom.

Final atomic positional co-ordinates, with e.s.d.s in parentheses, are listed in Tables 1 and 2. Atomic thermal parameters, and observed and calculated structure factors, are listed in Supplementary Publication No. SUP 23079 (25 pp.).*

TABLE 1

Final atomic positional co-ordinates and equivalent isotropic thermal parameters B_{eq}(Å^2) for non-hydrogen atoms of $[Tc(S_2CNEt_2)_2N]$

Atom	X/a	Y/b	Z/c	B_{eq}*
Tc	0.233 20(3)	0.110 90(5)	0.735 77(4)	3.63
S(1)	0.133 8(1)	0.122 9(2)	0.852 0(1)	4.55
S(2)	0.072 5(1)	0.109 7(2)	0.619 0(1)	4.88
S(3)	0.357 0(1)	0.267 7(2)	0.843 5(1)	3.96
S(4)	0.292 4(1)	0.246 0(2)	0.610 2(1)	4.04
N(1)	−0.048 9(4)	0.165 3(8)	0.733 8(5)	5.24
N(2)	0.426 9(3)	0.439 2(6)	0.715 7(4)	3.86
N(3)	0.275 3(4)	−0.051 3(7)	0.741 9(5)	5.26
C(1)	0.037 5(4)	0.131 3(8)	0.734 1(6)	4.68
C(2)	−0.074 5(6)	0.180 7(11)	0.835 3(8)	6.01
C(3)	−0.110 7(18)	0.041 8(25)	0.864 2(13)	9.75
C(4)	−0.126 7(6)	0.191 1(11)	0.627 1(8)	6.28
C(5)	−0.181 9(9)	0.058 9(15)	0.582 0(10)	7.70
C(6)	0.368 0(4)	0.333 3(7)	0.721 2(5)	3.51
C(7)	0.489 2(5)	0.510 5(9)	0.814 6(7)	4.91
C(8)	0.443 8(7)	0.629 4(11)	0.858 8(9)	6.37
C(9)	0.430 5(6)	0.493 5(9)	0.608 5(7)	5.13
C(10)	0.359 9(9)	0.614 9(13)	0.562 3(10)	7.09

* Calculated from the refined anisotropic thermal parameters (deposited), $B_{eq} = 8\pi^2U_{eq}$.

TABLE 2

Final hydrogen-atom positional co-ordinates and isotropic thermal parameters for $[Tc(S_2CNEt_2)_2N]$

Atom [a]	X/a	Y/b	Z/c	10^2U [b]
H(2A)	−0.144(9)	0.218(14)	0.814(9)	16(5)
H(2B)	−0.013(6)	0.213(10)	0.903(7)	11(3)
H(3A)	−0.159(9)	0.103(13)	0.919(11)	16(5)
H(3B)	−0.116(8)	−0.017(12)	0.801(9)	12(4)
H(3C)	−0.093(5)	0.033(9)	0.903(6)	3(2)
H(4A)	−0.185(7)	0.251(11)	0.636(7)	12(3)
H(4B)	−0.094(7)	0.234(11)	0.555(8)	13(4)
H(5A)	−0.132(5)	0.035(7)	0.627(5)	2(1)
H(5B)	−0.212(8)	0.013(11)	0.628(8)	11(4)
H(5C)	−0.113(16)	−0.048(24)	0.605(17)	31(11)
H(7A)	0.522(6)	0.434(9)	0.871(6)	8(2)
H(7B)	0.545(5)	0.548(8)	0.800(5)	6(2)
H(8A)	0.414(8)	0.698(14)	0.782(10)	15(5)
H(8B)	0.381(6)	0.600(8)	0.862(6)	8(2)
H(8C)	0.499(7)	0.671(11)	0.928(7)	11(3)
H(9A)	0.420(5)	0.416(8)	0.556(6)	7(2)
H(9B)	0.496(6)	0.535(10)	0.615(7)	9(3)
H(10A)	0.371(9)	0.693(15)	0.623(11)	18(6)
H(10B)	0.358(7)	0.641(12)	0.489(9)	12(4)
H(10C)	0.305(6)	0.575(10)	0.574(7)	9(3)

[a] Hydrogen atoms are given the same number as the carbon atom to which they are attached. [b] Defined by $T = \exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

Neutral atom scattering-factor curves for C, N, and S were taken from ref. 6, that for neutral Tc from ref. 7, and that for H from ref. 8. Real and imaginary anomalous-dispersion corrections were applied to the non-hydrogen atoms. Structure determination and refinement were performed with the SHELX-76 program system[9] on a VAX11/780 computer at the La Trobe University Computer Centre.

RESULTS AND DISCUSSION

The molecular geometry and atom numbering of the $[Tc(S_2CNEt_2)_2N]$ molecule are shown in the Figure. Interatomic bond distances and angles, with estimated standard deviations derived from the refinement, are given in Tables 3 and 4. Intra- and inter-molecular contact distances are given in Table 5.

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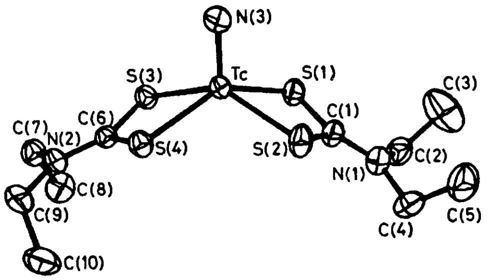
* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

The structure consists of discrete molecules of $[Tc(S_2CNEt_2)_2N]$, each containing a terminal N^{3-} group. The most interesting feature of the molecule is the Tc≡N bond. Although nitrido-complexes are known for many of the transition metals[10] including molybdenum, tungsten, rhenium, ruthenium, and osmium, this is the first report of a nitrido-complex of technetium.[10,11] It is also the first characterisation of a dithiocarbamato-complex of technetium.



An ORTEP (C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965) drawing of the $[Tc(S_2CNEt_2)_2N]$ molecule. The thermal ellipsoids are constructed at the 30% probability level

TABLE 3

Interatomic bond distances (Å) in $[Tc(S_2CNEt_2)_2N]$

Tc–N(3)	1.604(6)	C(2)–H(2A)	1.04(12)
Tc–S(1)	2.404(2)	C(2)–H(2B)	1.09(9)
Tc–S(2)	2.392(2)	C(3)–H(3A)	1.28(13)
Tc–S(3)	2.404(2)	C(3)–H(3B)	0.96(10)
Tc–S(4)	2.405(2)	C(3)–H(3C)	0.49(7)
S(1)–C(1)	1.734(7)	C(4)–H(4A)	1.06(10)
S(2)–C(1)	1.725(8)	C(4)–H(4B)	1.24(10)
S(3)–C(6)	1.738(6)	C(5)–H(5A)	0.82(6)
S(4)–C(6)	1.716(6)	C(5)–H(5B)	0.94(11)
N(1)–C(1)	1.317(9)	C(5)–H(5C)	1.38(22)
N(1)–C(2)	1.475(10)	C(7)–H(7A)	1.02(8)
N(1)–C(4)	1.514(10)	C(7)–H(7B)	0.97(7)
N(2)–C(6)	1.321(7)	C(8)–H(8A)	1.14(12)
N(2)–C(7)	1.474(8)	C(8)–H(8B)	0.98(9)
N(2)–C(9)	1.482(9)	C(8)–H(8C)	1.08(9)
C(2)–C(3)	1.472(20)	C(9)–H(9A)	0.96(8)
C(4)–C(5)	1.476(15)	C(9)–H(9B)	1.02(9)
C(7)–C(8)	1.483(12)	C(10)–H(10A)	1.03(14)
C(9)–C(10)	1.517(13)	C(10)–H(10B)	0.97(10)
		C(10)–H(10C)	0.95(9)

TABLE 4

Bond angles (°) in $[Tc(S_2CNEt_2)_2N]$

S(1)–Tc–N(3)	108.4(2)	C(1)–N(1)–C(4)	120.5(7)
S(2)–Tc–N(3)	108.9(2)	C(2)–N(1)–C(4)	117.1(7)
S(3)–Tc–N(3)	108.0(2)	C(6)–N(2)–C(7)	121.8(5)
S(4)–Tc–N(3)	107.0(2)	C(6)–N(2)–C(9)	120.7(5)
S(1)–Tc–S(2)	73.0(1)	C(7)–N(2)–C(9)	117.5(6)
S(3)–Tc–S(4)	73.0(1)	S(1)–C(1)–S(2)	111.2(4)
S(1)–Tc–S(3)	96.9(1)	S(1)–C(1)–N(1)	123.4(6)
S(2)–Tc–S(4)	94.6(1)	S(2)–C(1)–N(1)	125.1(6)
S(1)–Tc–S(4)	144.6(1)	N(1)–C(2)–C(3)	110.8(10)
S(2)–Tc–S(3)	143.1(1)	N(1)–C(4)–C(5)	113.8(8)
Tc–S(1)–C(1)	87.4(2)	S(3)–C(6)–S(4)	111.9(3)
Tc–S(2)–C(1)	88.0(2)	S(3)–C(6)–N(2)	123.4(4)
Tc–S(3)–C(6)	87.3(2)	S(4)–C(6)–N(2)	124.7(5)
Tc–S(4)–C(6)	87.7(2)	N(2)–C(7)–C(8)	114.8(6)
C(1)–N(1)–C(2)	122.4(7)	N(2)–C(9)–C(10)	113.1(7)

The compound $[Tc(S_2CNEt_2)_2N]$ is isostructural with the rhenium analogue $[Re(S_2CNEt_2)_2N]$,[12] which is perhaps not surprising considering the chemistry of the two metals is similar in many respects. Interest therefore focuses on a detailed comparison of the geometries of the two molecules, and in particular of the M≡N bond characteristics. The Tc≡N distance is found to be 1.604(6) whereas the Re≡N distance is longer at 1.656(8) Å, a result expected by a simple consideration of the relative radii of the technetium(V) and rhenium(V) ions. However, Re–N(nitrido) bond distances show a large variation,[10] from 1.53 Å in $K_2[ReN(NC)_4]\cdot H_2O$ in which the nitrogen atom asymmetrically bridges two rhenium atoms,[13] to 1.788(11) Å in $[ReNCl_2(PEt_2Ph)_3]$.[14] In $[ReNCl_2(PPh_3)_2]$, the Re≡N distance is 1.603(9) Å,[15] similar to the Tc≡N distance reported here. It is proposed[10] that the large variation in Re^V≡N bond distances is steric in origin with a concomitant variation in the degree of ligand-to-metal π donation. It would be of interest to determine whether a similar variation exists in Tc^V≡N bond lengths.

TABLE 5

Selected intra- and inter-molecular contact distances (Å) in $[Tc(S_2CNEt_2)_2N]$.* The latter are given within the limits of the contact radii: Tc, 2.2; S, 2.0; N, C, 1.8 Å

Tc · · · C(1)	2.900	S(2) · · · S(4)	3.525
Tc · · · C(6)	2.900	S(3) · · · S(4)	2.862
N(3) · · · S(1)	3.284	S(2) · · · S(2^{I})	3.738
N(3) · · · S(2)	3.283	S(1) · · · S(4^{II})	3.631
N(3) · · · S(3)	3.276	S(3) · · · S(4^{II})	3.838
N(3) · · · S(4)	3.258	S(2) · · · C(5^{I})	3.780
S(1) · · · S(2)	2.854	S(4) · · · C(5^{I})	3.754
S(1) · · · S(3)	3.597	S(4) · · · C(7^{III})	3.760

* Roman numeral superscripts refer to the following co-ordinate transformations: I $-x, -y, 1-z$; II $x, \frac{1}{2}-y, \frac{1}{2}+z$; III $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$.

Infrared absorptions attributable to the Re≡N stretching frequency occur in the region 1 000—1 100 cm^{-1}.[16] In the case of $[Tc(S_2CNEt_2)_2N]$, as well as those i.r. absorptions due to the dithiocarbamato-ligand, there is a strong absorption at 1 070 cm^{-1} which we assign to the Tc≡N stretching frequency.

The technetium atom in $[Tc(S_2CNEt_2)_2N]$ is in a distorted square-pyramidal environment, with the nitrogen atom in the apical position and four sulphur atoms forming the base. The Tc–S distances range between 2.392(2) and 2.405(2) Å whereas in $[Re(S_2CNEt_2)_2N]$ the Re–S distances are in the range 2.381(2)—2.391(2) Å.[12] This indicates that a simple rationalisation of bond lengths with expected ionic radii is not adequate. In this instance, presumably the ability of the ligand donor atoms to compete for the available *s*, *p*, *d*, and *f* valence orbitals of the metal atoms is affected by both the radial extents of those orbitals and by the steric constraints imposed by the bidentate S_2CNEt_2 ligands. The technetium atom in $[Tc(S_2CNEt_2)_2N]$ is 0.745(1) Å above the plane of the four sulphur donor atoms (Table 6), whereas the rhenium atom in $[Re(S_2CNEt_2)_2N]$ is 0.727 Å out of the plane. The Tc–S bond distances in $[Tc(S_2CNEt_2)_2N]$ are slightly greater than those found in $[NBu^n_4][Tc(SOCCH_2S)_2O]$[17]

TABLE 6

Planarity of groups of atoms within the [Tc(S_2CNEt$_2$)$_2$N] molecule and distances (Å) from least-squares planes

Atoms defining plane	Mean deviation of atoms in plane	Maximum deviation of atoms in plane	Atom out of the plane	Perpendicular distance from the plane
S(1),S(2),S(3),S(4)	0.014	0.014(2)	Tc	0.745(1)
S(1),S(2),C(1),N(1),C(2),C(4)	0.047	0.070(10)	Tc	0.374(1)
			C(3)	1.43(2)
			C(5)	1.25(1)
S(3),S(4),C(6),N(2),C(7),C(9)	0.009	0.015(9)	Tc	0.124(1)
			C(8)	1.34(1)
			C(10)	1.42(1)

[Tc–S 2.303(3) and 2.336(3) Å] and in an oxotechnetium(V) bis(dithiolate) complex[18] [Tc–S 2.299(4)—2.313(4) Å].

The S_2CNEt$_2$ ligands adopt the usual geometry with planar S_2CNC_2 segments (Table 6). The angle between the two S_2CNEt$_2$ planes is 59.4°, compared with 60° in [Re(S_2CNEt$_2$)$_2$N].[12] There is evidence from the refinement for disorder in the terminal methyl group of atom C(3). The positional co-ordinates of C(3) and of its bonded hydrogen atom H(3B) were the slowest variables to converge during the least-squares refinement. Moreover, the U_{11} and U_{22} parameters of the anisotropic thermal ellipsoid of C(3) were relatively large [0.24(2) and 0.15(1) Å^2 respectively]. The C(3)–H(3C) distance (Table 3) was also unacceptably short.

The molecules of [Tc(S_2CNEt$_2$)$_2$N] pack in the unit cell in an analogous fashion to the isostructural [Re(S_2CNEt$_2$)$_2$N].[12] There are no contacts of significance between the technetium atom and the neighbouring molecules.

The source of the nitrido-nitrogen atom is of interest. It presumably originates from the deprotonation of hydrazine, a method which has previously been utilised in the preparation of rhenium(V) nitrido-complexes.[10,16] However, the analogous [Re(S_2CNEt$_2$)$_2$N] complex was prepared by reaction of Na[S_2CNEt$_2$] with [ReNCl$_2$(PPh$_3$)$_2$].[19]

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