Notes

N-Thionitrosamine Complexes: Substitution Reactions of Complexes $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ (M = Ru or Os) and the Crystal Structure of $[OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ ‡

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The substitution reactions of $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ (M = Ru or Os) with a variety of ligands (azide, carbon monoxide, 2-xylyl isocyanide, or t-butyl cyanide) are described and rationalized with reference to an *X*-ray structure analysis of $[OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ which reveals a comparatively short Os–S bond [2.411(2) Å] and a long Os–Cl bond [2.476(3) Å]. The thionitrosodimethylamine ligand is essentially planar, co-ordinated to osmium with its molecular plane almost perpendicular to the phosphorus–phosphorus vector.

N-Thionitrosamines, $R_2N{-}N{=}S$, provide rare examples of compounds which contain multiple bonds between nitrogen and bivalent sulphur.[1] Despite their instability in the free state, evidence continues to accumulate suggesting that *N*-thionitrosamines may co-ordinate to a wide range of transition metals in a variety of oxidation states and *d* configurations[2–5] and, in doing so, attain a degree of stability.

We have recently prepared a number of complexes[5] containing *N*-thionitrosodimethylamine ($Me_2N{-}NS$) bound to ruthenium, osmium, and iridium. Herein we discuss the substitution reactions of the σ-aryl complexes $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ (M = Ru or Os) with selected ligands as well as the reactivity of $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2L]$ (L = 2,1,3-benzothiadiazole, 2,1,3-benzoselenadiazole, sulphur dioxide, carbon monoxide, or 2-xylyl isocyanide) towards *N*-thionitrosodimethylamine. The results are interpreted in terms of structural information obtained from a crystal-structure analysis of the osmium complex $[OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$.

Results and Discussion

The *N*-thionitrosodimethylamine complexes $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ [M = Ru (**1a**) or Os (**1b**)] may be prepared in high yield by treating the co-ordinatively unsaturated 16-electron compounds $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2]$[6] with the ligand $Me_2N{-}NS$ (Scheme 1).[5] The complexes are indefinitely stable, in contrast to the free molecule $Me_2N{-}NS$.[1] The osmium complex (**1b**) has similarly been obtained from the 18-electron precursor complexes $[OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2L]$ containing labile ligands, L, such as SO_2, 2,1,3-benzothiadiazole, and 2,1,3-benzoselenadiazole. While these complexes react rapidly with $Me_2N{-}NS$ to provide (**1b**) the corresponding 18-electron complexes containing CO and 2-xylyl isocyanide fail to react within 1 week. Indeed these complexes are rapidly formed upon exposure of (**1b**) to the appropriate ligand, CO or 2-xylyl isocyanide (Scheme 1).

Substitution reactions are not limited to the thionitrosamine ligand, however:[5] reaction of $[RuCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ (**1a**) with t-butyl cyanide (pivalonitrile) in the presence of a non-co-ordinating anion (PF_6^-) leads to the salt $[Ru(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(NCBu^t)(SNNMe_2)]PF_6$. Treatment of (**1a**) with sodium azide, NaN_3, provides the azido complex $[Ru(N_3)(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ in high yield. The latter reaction is catalysed by pivalonitrile and presumably proceeds *via* the cation $[Ru(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(NCBu^t)(SNNMe_2)]^+$.

The substitutive reactivity observed for the complexes $[MCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ (Scheme 1) might be rationalised by reference to structural parameters of the complexes. It was possible to obtain crystals of (**1b**) and a crystal structure determination was performed.

Crystal and Molecular Structure of $[OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$ (**1b**).—The molecular structure of complex (**1b**) is presented in the Figure. The osmium atom is octahedrally co-ordinated by its six ligands. The two phosphine ligands, the chloride and carbonyl groups, and the *p*-tolyl and thionitrosamine ligands occupy mutually *trans* co-ordination sites in the octahedron. Bond lengths and angles in the co-ordination sphere of the osmium atom and in the $SNNMe_2$ ligand are given in Table 1.

The *N*-thionitrosodimethylamine ligand is planar. Its orientation towards the rest of the molecule is *trans* (*E*) with respect to the nitrogen–sulphur bond [N(1)–S(1)] and is characterised by an eclipsed position of this bond and the carbonyl ligand [Os–S–N(1)–N(2) −170° and C(3)–Os–S–N(1) 20.3°].

In addition to the major molecular conformation (α, *ca.* 60%), a second minor conformation (β, *ca.* 40%) is present in the crystal in which the chloride and thionitrosamine ligands are eclipsed (Figure). The solid-state i.r. spectra of complexes (**1a**) and (**1b**) show two carbonyl absorptions which may derive from

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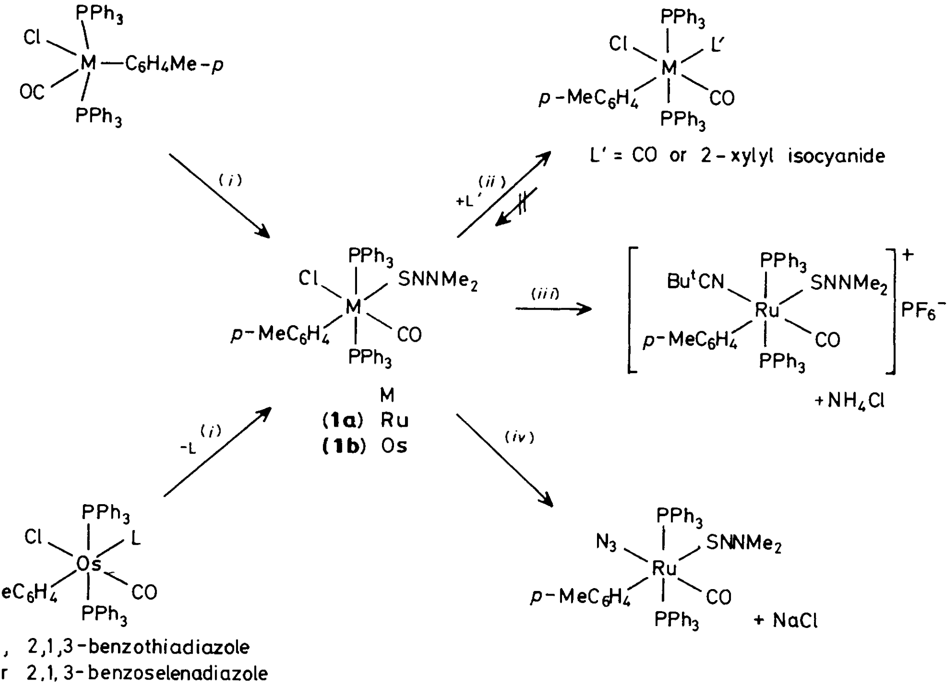
‡ Carbonylchloro(dimethylthionitrosamine-*S*)*p*-tolylbis(triphenylphosphine)osmium.

Supplementary data available: further information regarding the crystallographic study may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, Germany by quoting the number CSD-52376, the authors, and the complete literature citation.



Scheme 1. (*i*) Me_2N-NS; (*ii*) $-Me_2N-NS$; (*iii*) Bu^{t}CN, NH_4PF_6; (*iv*) NaN_3, Bu^{t}CN

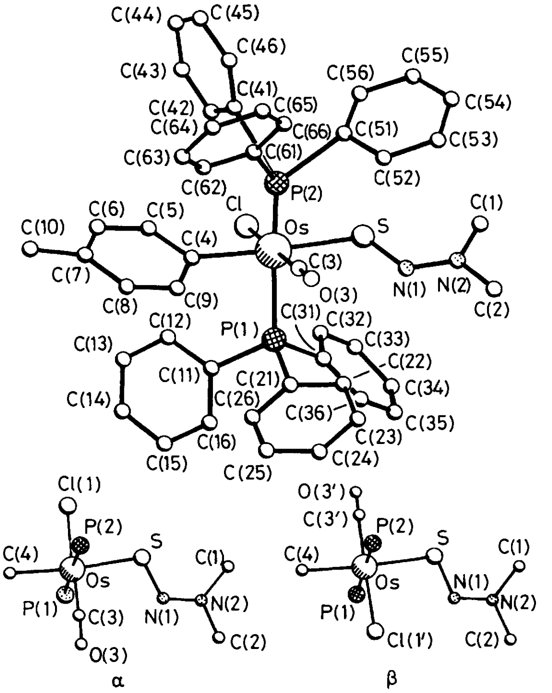
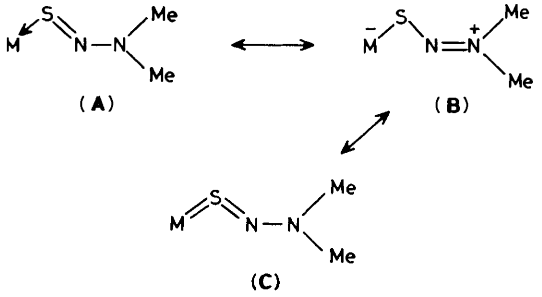


Figure. Molecular structure of $[OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)]$. Two conformations (α and β) are present in the crystal

these two conformers since solution i.r. measurements reveal only one absorption [(**1b**): ν(CO) 1 921 and 1 908 cm^{-1} in Nujol, 1 910 cm^{-1} in CH_2Cl_2 solution].[5]

The bonding in metal-co-ordinated thionitrosamines may be described by the canonical forms (**A**)–(**C**) with a major contribution from resonance form (**B**) (Scheme 2). The N(1)–N(2) distance [1.293(10) Å] is *ca.* 0.05 Å longer than that of a typical N=N double bond, whereas the S–N(1) bond [1.616(7) Å] is about 0.1 Å longer than a S=N double bond (1.49—1.57 Å in various sulphur di-imides[7–14]). The multiple-bond character of the nitrogen–nitrogen bond explains the high barrier to rotation about N(1)–N(2) observed in ^1H n.m.r. studies of (**1b**) which reveal significantly different chemical environments for the two methyl groups.[5]



Scheme 2.

A comparison of the *N*-thionitrosodimethylamine ligand in (**1b**) with that recently reported in $[Cr(CO)_5(SNNMe_2)]$[2] and *cis*-$[PdCl_2(AsPh_3)(SNNMe_2)]$[4] shows a slight shortening of the N(1)–S bond by about 0.02 Å, accompanied by a corresponding lengthening of the N(1)–N(2) bond of similar magnitude. This is consistent with the pronounced ability of the ruthenium(II) and osmium(II) centres for back donation into ligand π orbitals [valence-bond form (**C**)]. In all three compounds the N–C bond *trans* to sulphur is longer than that *cis* to sulphur.

The osmium–sulphur bond [2.411(2) Å] is longer than the Os–S bond to the coplanar SO_2 ligand in $[OsCl(H)(CO)\{P(C_6H_{11})_3\}_2(SO_2)]$ [2.239(3) Å].[15]

The Os–Cl bond length [2.476(3) Å, major chloride site] is considerably greater than the sum of the covalent radii (1.33 + 0.99 = 2.32 Å).[16] This might be explained by a *cis*-labilising effect, *i.e.* the accumulation of electron density in orbitals of π symmetry *cis* to the halide which results in a weakening of the osmium–chloride interaction.

Table 1. Selected structural parameters for [OsCl(C_6H_4Me-*p*)(CO)-(PPh_3)$_2$($SNNMe_2$)] (**1b**). Bond distances (Å) and angles (°) which are different in the two conformations (α and β) of the crystal, are also given for the minor conformation

	Major conformation (α, *ca.* 60%)	Minor conformation (β, *ca.* 40%)
Osmium co-ordination		
Os–Cl	2.476(3)	2.507(9)
Os–P(1)	2.392(1)	
Os–P(2)	2.430(1)	
Os–S	2.411(2)	
Os–C(3)	1.798(15)	1.950(32)
Os–C(4)	2.117(7)	
N-Thionitrosamine ligand		
S–N(1)	1.616(7)	
N(1)–N(2)	1.293(10)	
N(2)–C(1)	1.446(12)	
N(2)–C(2)	1.465(13)	
Osmium co-ordination		
Cl–Os–P(1)	87.9(1)	93.3(2)
Cl–Os–P(2)	95.8(1)	83.0(2)
Cl–Os–S	81.0(1)	93.5(2)
Cl–Os–C(3)	175.3(5)	175.4(12)
Cl–Os–C(4)	94.3(2)	91.3(2)
P(1)–Os–P(2)	176.3(1)	
P(1)–Os–S	90.9(1)	
P(1)–Os–C(3)	91.0(5)	90.0(11)
P(1)–Os–C(4)	91.3(2)	
P(2)–Os–S	89.8(1)	
P(2)–Os–C(3)	85.3(5)	93.7(11)
P(2)–Os–C(4)	88.3(2)	
S–Os–C(3)	94.5(5)	83.2(13)
S–Os–C(4)	174.7(2)	
C(3)–Os–C(4)	90.3(6)	91.9(13)
N-Thionitrosamine ligand		
Os–S–N(1)	107.2(3)	
S–N(1)–N(2)	119.6(6)	
N(1)–N(2)–C(1)	123.5(7)	
N(1)–N(2)–C(2)	116.9(7)	
C(1)–N(2)–C(2)	119.5(7)	

Conclusions

Substitution reactions of [MCl(C_6H_4Me-*p*)(CO)(PPh_3)$_2$-($SNNMe_2$)] [M = Ru (**1a**) or Os (**1b**)] lead to displacement of either the *N*-thionitrosodimethylamine or the chloro ligand. The lability of σ-donating ligands L in [OsCl(C_6H_4Me-*p*)-(CO)(PPh_3)$_2$L] complexes can be explained by the influence of the σ-tolyl ligand which exerts a strong *trans* effect. It appears that only good π acids such as carbon monoxide and 2-xylyl isocyanide are firmly bound to the metal. The importance of the metal-to-ligand back bonding becomes also apparent in the structural parameters of [OsCl(C_6H_4Me-*p*)(CO)(PPh_3)$_2$-($SNNMe_2$)] (**1b**): the Os–S distance [2.411(2) Å] may indicate some multiple bonding, and the orientation of the planar *N*-thionitrosamine ligand almost perpendicular to the P–Os–P vector is in agreement with a π component to the metal–sulphur bond. This conformation in which the ligand lies in the equatorial plane of the octahedron is known to maximise π interactions and is similarly observed in related complexes containing π-bound ligands, *e.g.* [$OsCl_2$(CO)(PPh_3)$_2$(CCl_2)],[17] [$OsCl_2$(CO)-(PPh_3)$_2$(CHPh)],[18] and [OsCl(H)(CO){P(C_6H_{11})$_3$}$_2$(SO_2)].[15] According to the reactions summarised for [OsCl(C_6H_4Me-*p*)-(CO)(PPh_3)$_2$L] complexes in Scheme 1, the π-acid capacity of the ligand L appears to increase in the order SO_2 < Me_2N–NS < CO.

Substitution of the chloro ligand in complex (**1b**) is apparently facilitated by *cis* labilisation through both the tolyl and the thionitrosamine ligand, in agreement with the long Os–Cl bond distance [2.476(3) Å].

Experimental

The syntheses and spectroscopic characterizations of the *N*-thionitrosodimethylamine complexes have been described previously.[5]

Crystallography.—Crystals of [OsCl(C_6H_4Me-*p*)(CO)-(PPh_3)$_2$($SNNMe_2$)] (**1b**) for *X*-ray studies were obtained by slow diffusion of a n-hexane layer into a dichloromethane solution over a period of 4 weeks. The crystal chosen for measurement (0.5 × 0.4 × 0.4 mm) was mounted in a glass capillary under argon. The determination of the lattice constants and the data collection were carried out on a computer-controlled diffractometer (Enraf-Nonius CAD 4) employing Mo-K_α radiation in conjuction with a graphite monochromator. The determination of the lattice constants was based on the orientational parameters of 22 reflections ($9.4 \leqslant \theta \leqslant 23..2°$).

Crystal data. $C_{46}H_{43}ClN_2OOsP_2S$, $M = 959.63$, monoclinic, space group $P2_1/n$, $a = 12.235(4)$, $b = 24.305(4)$, $c = 14.066(2)$ Å, $\beta = 103.22(2)°$, $U = 4\,070.0$ Å^3, $D_m = 1.54$ g cm^{-3}, $Z = 4$, $D_c = 1.567$ g cm^{-3}, $F(000) = 1\,920$, μ(Mo-K_α) = 32.06 cm^{-1}.

On the above-mentioned single-crystal diffractometer, the intensities of 6 237 independent reflections were measured using the ω–2θ mode in the range $0 < \theta < 25°$. The 5 508 observed reflections ($I > 2\sigma I$) were subjected to Lorentz and absorption corrections. The empirical parameters used for absorption correction[19] were derived from ψ scans of nine selected reflections.

The heavy-atom position was located by a Patterson synthesis, and the remaining non-hydrogen atoms were located in a subsequent Fourier difference synthesis. The structure was refined first with isotropic and then with anisotropic thermal parameters using a least-squares procedure with overlapping partial cycles.

In the refinement process it became obvious that a structurally unreasonable C–O bond distance indicated a statistical disorder which could be identified through a Fourier difference synthesis. The disorder derives from the superposition of two molecular conformations (α and β) which are formally related by the exchange of chloride and carbonyl ligands. The disorder problem was handled by refining the two chloride sites with anisotropic thermal parameters and the C(3) and O(3) positions with isotropic thermal parameters.

In the final stages of the structure refinement a Fourier difference synthesis revealed the locations of the hydrogen atoms which were subsequently refined with isotropic thermal parameters. The refinement converged to an *R* factor of 0.034 $\{R' = 0.036;\ w = k/[\sigma^2(F_o) + 0.000\,03|F_o|^2]\}$. In the final refinement step 72 reflections with $|\Delta F| = ||F_o| - |F_c|| > 15$ were eliminated.

The majority of the computer calculations were carried out with the program SHELX 76[20] and the *X*-RAY 76 program system[21] using a VAX 11/782 computer. The atomic form factors not contained in the SHELX 76 program were obtained from ref. 22.

The atomic co-ordinates are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 2. Relative atomic co-ordinates of the non-hydrogen atoms of [$OsCl(C_6H_4Me\text{-}p)(CO)(PPh_3)_2(SNNMe_2)$] (**1b**). The atoms denoted by an asterisk (*) were refined only with isotropic thermal parameters. Site occupancies Cl(1), C(3), O(3), 0.6; Cl(1′), C(3′), O(3′), 1—0.6

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os	0.165 59(2)	0.125 52(1)	0.261 77(2)	C(23)	0.327 6(7)	0.080 4(4)	−0.043 7(7)
Cl(1)	0.249 1(2)	0.137 4(1)	0.438 4(2)	C(24)	0.346 3(6)	0.126 1(5)	−0.093 4(6)
Cl(1′)	0.080 5(5)	0.103 5(3)	0.086 2(7)	C(25)	0.363 3(6)	0.175 6(4)	−0.047 4(6)
P(1)	0.350 0(1)	0.136 7(1)	0.234 1(1)	C(26)	0.366 3(5)	0.179 8(3)	0.052 0(6)
P(2)	−0.026 3(1)	0.113 6(1)	0.278 5(1)	C(31)	0.456 7(5)	0.084 9(3)	0.289 3(5)
S	0.203 9(1)	0.030 4(1)	0.305 8(1)	C(32)	0.480 3(6)	0.078 3(3)	0.389 5(6)
N(1)	0.209 0(5)	−0.002 4(3)	0.207 0(5)	C(33)	0.564 1(6)	0.042 9(4)	0.435 9(6)
N(2)	0.211 7(5)	−0.055 6(3)	0.207 6(5)	C(34)	0.625 4(6)	0.012 9(3)	0.383 8(7)
O(3)*	0.069 8(13)	0.105 3(7)	0.053 4(10)	C(35)	0.604 0(7)	0.019 0(4)	0.286 3(7)
O(3′)*	0.263 0(27)	0.144 7(15)	0.467 0(21)	C(36)	0.520 8(6)	0.055 5(3)	0.238 4(6)
C(1)	0.207 5(7)	−0.088 5(3)	0.292 3(7)	C(41)	−0.077 8(5)	0.140 3(3)	0.382 9(5)
C(2)	0.213 6(9)	−0.082 9(4)	0.115 1(8)	C(42)	−0.005 8(5)	0.157 7(3)	0.468 1(5)
C(3)*	0.109 4(13)	0.111 3(7)	0.134 4(11)	C(43)	−0.048 4(6)	0.176 6(3)	0.546 7(6)
C(3′)*	0.224 8(30)	0.137 7(18)	0.401 2(24)	C(44)	−0.163 1(6)	0.177 9(3)	0.537 8(6)
C(4)	0.130 9(5)	0.210 3(3)	0.236 7(5)	C(45)	−0.234 2(6)	0.159 5(4)	0.454 8(6)
C(5)	0.107 2(5)	0.245 6(3)	0.307 4(5)	C(46)	−0.193 0(6)	0.140 9(4)	0.378 0(5)
C(6)	0.067 3(6)	0.298 8(3)	0.286 1(6)	C(51)	−0.062 4(5)	0.040 4(3)	0.281 4(5)
C(7)	0.048 5(5)	0.321 1(3)	0.192 0(6)	C(52)	−0.061 3(5)	0.008 1(3)	0.198 9(6)
C(8)	0.075 7(6)	0.287 8(3)	0.120 9(5)	C(53)	−0.082 5(6)	−0.048 4(3)	0.198 3(7)
C(9)	0.117 7(5)	0.234 9(3)	0.143 7(5)	C(54)	−0.101 9(6)	−0.072 2(3)	0.282 6(8)
C(10)	−0.005 7(6)	0.377 0(4)	0.168 0(6)	C(55)	−0.100 0(6)	−0.042 1(3)	0.364 8(7)
C(11)	0.429 9(5)	0.199 2(3)	0.279 2(5)	C(56)	−0.080 5(6)	0.014 1(3)	0.363 8(6)
C(12)	0.395 1(5)	0.235 4(3)	0.342 0(6)	C(61)	−0.139 4(5)	0.140 1(3)	0.179 5(5)
C(13)	0.461 9(6)	0.280 2(3)	0.381 0(6)	C(62)	−0.139 7(5)	0.194 7(3)	0.156 7(6)
C(14)	0.561 8(6)	0.288 9(3)	0.357 8(6)	C(63)	−0.230 1(6)	0.219 2(4)	0.091 3(7)
C(15)	0.599 0(5)	0.253 4(3)	0.294 6(6)	C(64)	−0.321 8(6)	0.188 5(4)	0.049 7(6)
C(16)	0.533 8(5)	0.208 7(3)	0.256 3(5)	C(65)	−0.322 4(5)	0.134 9(4)	0.071 1(6)
C(21)	0.349 3(5)	0.134 5(3)	0.103 8(5)	C(66)	−0.231 3(6)	0.110 2(3)	0.134 7(5)
C(22)	0.326 8(6)	0.084 3(3)	0.055 4(6)				

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