Preparation and Crystal Structure * of Trichloro(thionitrosyl)-bis(triphenylphosphine)osmium, $[Os(NS)Cl_3(PPh_3)_2]$

Herbert W. Roesky, Krishna K. Pandey, William Clegg, Mathias Noltemeyer, and George M. Sheldrick
Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

The compound $(NSCl)_3$ reacts with $[MCl_2(PPh_3)_3]$ (M = Os or Ru) in tetrahydrofuran to give the thionitrosyl complexes $[M(NS)Cl_3(PPh_3)_2]$ [M = Os (1) or Ru (2)]. Nitrosyl chloride or bromide converts (1) to the corresponding nitrosyl complex. Crystals of (1) are monoclinic, space group *I*2/*a*, with *a* = 1 615.9(6), *b* = 943.7(5), *c* = 2 250.6(10) pm, β = 103.02(3)°, and *Z* = 4. The structure was was refined to *R* = 0.042 for 2 076 diffractometer data. The osmium is octahedrally co-ordinated with the phosphines *cis* to the NS group; a crystallographic two-fold axis along the Cl–Os–N–S bonds imposes linearity at nitrogen, with Os–N 177.9(9), N–S 150.3(10), Os–P 245.9(2), Os–Cl(*cis*) 238.7(3), and Os–Cl(*trans*) 239.9(3) pm. Complex (2) is apparently isostructural, with *a* = 1 613.5(15), *b* = 941.8(4), *c* = 2 249.3(15) pm, and β = 102.94(3)°.

Thionitrosyl complexes of transition metals[1] have been prepared by (*a*) reactions of nitrido-complexes with sulphur,[2] sulphur halides,[2] or potassium thiocyanate,[3] (*b*) reactions of the compound $(NSCl)_3$, with transition-metal complexes,[4–8] (*c*) extraction of fluoride from NSF by Lewis acids,[9] and (*d*) reactions of $[NS]^+$ salts.[10] Infrared spectra suggest[6–8] that linear, bent, and bridged thionitrosyl groups are all possible, but the two *X*-ray diffraction studies reported so far, $[Cr(\eta^5\text{-}C_5H_5)(CO)_2(NS)]$[5] and $[Mo(NS)(S_2CNMe_2)_3]$,[11] found essentially linear M–N–S units. In this paper we report an improved synthesis and the crystal structure determination of $[Os(NS)Cl_3(PPh_3)_2]$ (1), together with reactions of (1) with nitrosyl halides. We have also prepared $[Ru(NS)Cl_3(PPh_3)_2]$ (2) by an analogous reaction; although the crystals of (2) were too small for crystal structure determination, it proved possible to determine the unit cell.

Experimental

All reactions were performed under nitrogen; solvents were dried, distilled, and deaerated just prior to use. The compounds $[OsCl_2(PPh_3)_3]$,[12] NOCl,[13] and NOBr[14] were prepared by literature methods. I.r. spectra were recorded as KBr pellets on a Perkin-Elmer 511 spectrometer.

Preparation of $[Os(NS)Cl_3(PPh_3)_2]$ (1).—A solution of $(NSCl)_3$ (0.17 g, 0.70 mmol) in tetrahydrofuran (thf) (20 cm^3) was added dropwise to a stirred solution of $[OsCl_2(PPh_3)_3]$ (2.1 g, 2.0 mmol) in thf (100 cm^3) at room temperature, and the mixture stirred for a further 5 h. The resulting solution was evaporated under vacuum nearly to dryness and extracted with methylene chloride (30 cm^3). On addition of hot methanol (50 cm^3) to the methylene chloride solution, complex (1) separated out in the form of shiny green plates and yellowish orange needles. The solid product was filtered off, washed with methanol, and then diethyl ether, and dried *in vacuo* (yield 0.95 g, 55%). Recrystallisation from CH_2Cl_2–CH_3OH (1 : 2) converted the product entirely to the green form, m.p. > 250 °C (Found: C, 49.6; H, 3.6; Cl, 12.4; N, 1.7; S, 3.6. $C_{36}H_{30}Cl_3NOsP_2S$ requires C, 49.7; H, 3.45; Cl, 12.3; N, 1.6; S, 3.7%).

Preparation of $[Ru(NS)Cl_3(PPh_3)_2]$ (2).—In an analogous preparation, $(NSCl)_3$ (0.04 g, 0.17 mmol) in thf (20 cm^3) was added to $[RuCl_2(PPh_3)_3]$ (0.48 g, 0.4 mmol) in thf (75 cm^3) (yield 0.18 g, 46%). Orange-brown crystals of (2) (m.p. 192—194 °C) were obtained by recrystallisation from CH_2Cl_2–CH_3OH (1 : 3) (Found: C, 55.4; H, 4.0; Cl, 13.4; N, 2.1; S, 4.3. $C_{36}H_{30}Cl_3NP_2RuS$ requires C, 55.5; H, 3.8; Cl, 13.7; N, 1.9; S, 4.1%).

Reaction of (1) *with* NOCl.—A saturated solution of NOCl in CH_2Cl_2 (20 cm^3) was added dropwise to a stirred solution of (1) (0.2 g, 0.2 mmol) in CH_2Cl_2 (20 cm^3) and the mixture refluxed for 30 min. The volume was reduced to 10 cm^3 under reduced pressure, hot methanol (30 cm^3) added, and the resulting precipitate filtered off, washed with methanol and then diethyl ether, and dried *in vacuo* (Found: C, 50.9; H, 3.6; N, 1.6. $C_{36}H_{30}Cl_3NOOsP_2$ requires C, 50.8; H, 3.5; N, 1.65%). I.r.: ν(NO) at 1 848 cm^{-1}.

Reaction of (1) *with* NOBr.—A small amount (5 cm^3) of an approximately 2 mol dm^{-3} solution of NOBr in CH_2Cl_2 was added to (1) (0.2 g, 0.26 mmol) in CH_2Cl_2 (20 cm^3), and the product isolated as in the NOCl experiment (Found: C, 48.3; H, 3.4; N, 1.6. $C_{36}H_{30}BrCl_2NOOsP_2$ requires C, 48.3; H, 3.35; N, 1.55%). I.r.: ν(NO) at 1 845 cm^{-1}.

Crystal Data for (1).—$C_{36}H_{30}Cl_3NOsP_2S$, *M* = 867.2, monoclinic, space group *I*2/*a*, *a* = 1 615.9(6), *b* = 943.7(5), *c* = 2 250.6(10) pm, β = 103.02(3)°, *U* = 3.344 nm^3, *Z* = 4, D_c = 1.722 Mg m^{-3}, *F*(000) = 1 704, λ(Mo-K_α) = 71.069 pm, μ(Mo-K_α) = 4.24 mm^{-1}, crystal dimensions 0.4 × 0.2 × 0.08 mm. Conventional setting: *C*2/*c*, *a* = 2 457.2(11), *b* = 943.7(5), *c* = 2 250.6(10) pm, β = 140.15(3)°.

3 457 Reflections were measured by a profile-fitting pro-

---

* *Supplementary data available* (No. SUP 23836, 15 pp.): structure factors, H-atom co-ordinates, anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.

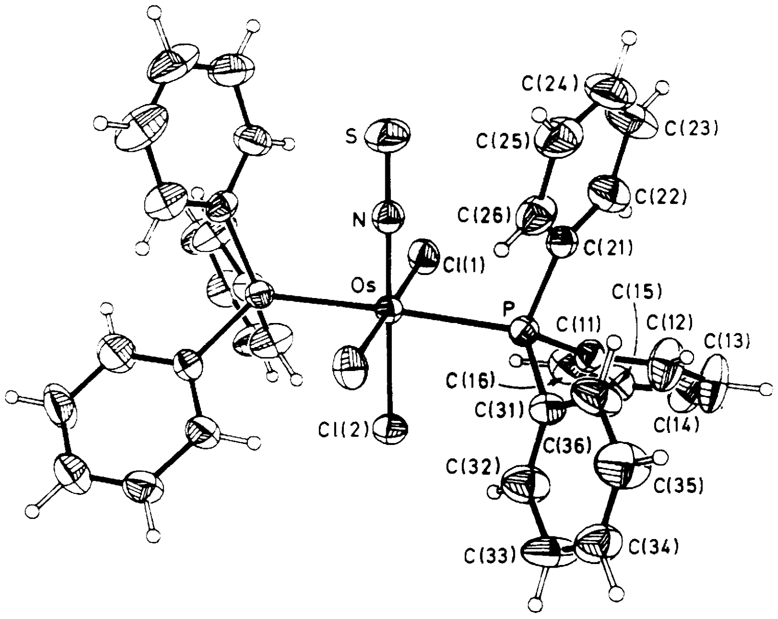

Figure. The molecule of $[Os(NS)Cl_3(PPh_3)_2]$ (1), with 50% probability thermal ellipsoids for the non-hydrogen atoms, and the unique atoms labelled

Table 1. Atomic parameters (× 10^4) with estimated standard deviations in parentheses for $[Os(NS)Cl_3(PPh_3)_2]$ (1)

Atom	*x*	*y*	*z*
Os	2 500	1 620(1)	0
N	2 500	−265(10)	0
S	2 500	−1 858(4)	0
Cl(1)	1 387(1)	1 607(2)	541(1)
Cl(2)	2 500	4 162(3)	0
P	3 627(1)	1 678(2)	939(1)
C(11)	3 451(5)	2 685(9)	1 594(4)
C(12)	4 075(6)	2 651(12)	2 128(4)
C(13)	3 978(7)	3 416(12)	2 633(5)
C(14)	3 267(6)	4 217(11)	2 611(4)
C(15)	2 656(6)	4 255(10)	2 095(4)
C(16)	2 740(6)	3 496(8)	1 577(4)
C(21)	3 828(4)	−131(8)	1 203(4)
C(22)	3 532(6)	−650(10)	1 693(4)
C(23)	3 616(7)	−2 085(11)	1 847(6)
C(24)	4 002(7)	−2 968(11)	1 528(6)
C(25)	4 294(6)	−2 494(11)	1 020(5)
C(26)	4 213(5)	−1 071(10)	869(4)
C(31)	4 674(5)	2 341(9)	884(4)
C(32)	4 741(6)	3 703(10)	694(5)
C(33)	5 535(6)	4 309(10)	711(5)
C(34)	6 244(6)	3 553(10)	904(5)
C(35)	6 192(6)	2 201(12)	1 096(6)
C(36)	5 413(6)	1 595(10)	1 089(5)

cedure [15] on a Stoe-Siemens four-circle diffractometer in the range $7 < 2\theta < 45°$. After Lorentz, polarisation, and semi-empirical absorption corrections, equivalent data were merged to yield 2 076 unique reflections with $F > 3\sigma(F)$ which were used for all calculations, performed with the SHELXTL system of programs (written by G. M. S.). The structure was solved by Patterson and Fourier methods, and refined with complex neutral-atom scattering factors, riding hydrogen atoms [C–H = 96 pm with H on the external C–C–C bisectors, common U(H) refined to 0.075(9) × 10^4 pm^2], the remaining atoms anisotropic, and weights $w^{-1} = [\sigma^2(F) + 0.0015 F^2]$ to $R' = 0.043$ ($R = 0.042$). A final difference map showed no peaks $> 10^{-6}$ e pm^3, and an analysis of variance showed no systematic trends with $|F|$ or sin θ. Final co-ordinates are given in Table 1 and bond lengths and angles in Table 2. The molecule of (1) is shown in the Figure.

Crystal Data for (2).—$C_{36}H_{30}Cl_3NP_2RuS$, $M = 778.1$, monoclinic, space group $I2/a$, $a = 1\,613.5(15)$, $b = 941.8(4)$, $c = 2\,249.3(15)$ pm, $\beta = 102.94(3)°$, $U = 3.331$ nm^3, $Z = 4$, $D_c = 1.55$ Mg m^{-3}, $F(000) = 1\,576$, μ(Mo-K_α) = 0.89 mm^{-1}, λ(Mo-K_α) = 71.069 pm. Conventional setting: $C2/c$, $a = 2\,457.1(15)$, $b = 941.8(4)$, $c = 2\,249.3(15)$ pm, $\beta = 140.21(3)°$.

Results and Discussion

Complex $[Os(NS)Cl_3(PPh_3)_2]$ (1) had been prepared previously [6] only in much lower yield by the reaction of $(NSCl)_3$ with $OsCl_3$ in the presence of PPh_3. The mixture of the green and yellowish orange isomers (or crystalline forms) of (1) shows strong i.r. bands at 1 310 and 1 290 cm^{-1} which are assigned to ν(NS). After recrystallisation, the band at 1 290 cm^{-1} disappeared and the other became stronger. The N–S ligand in (1) may be replaced by N–O by the action of nitrosyl halides; the products, $[Os(NO)XCl_2(PPh_3)_2]$ (X = Cl or Br), exhibit ν(NO) bands typical of Os^{II}–N–O systems.[16]

After the structure determination had been completed, it was noticed that both (1) and (2) were almost certainly isostructural with $[Ru(NO)Cl_3(PPh_3)_2]$ [space group $I2/a$ with $a = 1\,587.7(3)$, $b = 954.0(2)$, $c = 2\,232.6(4)$ pm, and $\beta = 102.79(1)°$ [17]], and therefore the calculations were repeated with the unconventional $I2/a$ setting employed for the ruthenium nitrosyl complex. This space group requires that a crystallographic two-fold axis passes through the octahedral complex, *i.e.* that the Cl–M–N–S (or Cl–M–N–O; M = Os or Ru) unit is linear, and that the triphenylphosphine ligands are *cis* to N–S (or N–O).

Molecular-orbital comparisons [18,19] of NS and NO indicate that the 7σ donor orbital of NS is antibonding in nature and *ca.* 3.8 eV higher in energy than the 5σ donor orbital of NO. On the other hand the 3π acceptor orbital of NS lies *ca.* 1.1 eV lower than the 2π acceptor orbital of NO. This suggests that

Table 2. Bond distances (pm) and angles (°) with estimated standard deviations in parentheses for [Os(NS)Cl$_3$(PPh$_3$)$_2$] (1)

Os–N	177.9(9)	Os–Cl(1)	238.7(3)
Os–Cl(2)	239.9(3)	Os–P	245.9(2)
N–S	150.3(10)	P–C(11)	183.0(9)
P–C(21)	181.3(8)	P–C(31)	183.5(8)
C(11)–C(12)	138.4(11)	C(11)–C(16)	137.4(12)
C(12)–C(13)	138.4(16)	C(13)–C(14)	136.7(15)
C(14)–C(15)	134.4(12)	C(15)–C(16)	140.2(13)
C(21)–C(22)	138.6(13)	C(21)–C(26)	139.7(13)
C(22)–C(23)	139.7(14)	C(23)–C(24)	134.2(17)
C(24)–C(25)	140.6(18)	C(25)–C(26)	138.4(14)
C(31)–C(32)	136.6(13)	C(31)–C(36)	137.3(12)
C(32)–C(33)	139.8(14)	C(33)–C(34)	133.7(13)
C(34)–C(35)	135.6(15)	C(35)–C(36)	138.0(14)
N–Os–Cl(1)	89.7(1)	N–Os–Cl(2)	180.0
Cl(1)–Os–Cl(2)	90.3(1)	N–Os–P	91.3(1)
Cl(1)–Os–P	93.4(1)	Cl(2)–Os–P	88.7(1)
P–Os–P′	177.4(1)	Cl(1)–Os–Cl(1′)	179.4(1)
		P–Os–Cl(1′)	86.6(1)
Os–N–S	180.0(1)	Os–P–C(11)	119.0(2)
Os–P–C(21)	107.7(2)	C(11)–P–C(21)	105.9(4)
Os–P–C(31)	117.7(3)	C(11)–P–C(31)	100.9(4)
C(21)–P–C(31)	104.1(4)	P–C(11)–C(12)	118.2(7)
P–C(11)–C(16)	123.1(6)	C(12)–C(11)–C(16)	118.6(8)
C(11)–C(12)–C(13)	120.3(9)	C(12)–C(13)–C(14)	120.6(9)
C(13)–C(14)–C(15)	119.5(10)	C(14)–C(15)–C(16)	121.0(9)
C(11)–C(16)–C(15)	119.9(8)	P–C(21)–C(22)	121.7(6)
P–C(21)–C(26)	119.3(7)	C(22)–C(21)–C(26)	118.7(8)
C(21)–C(22)–C(23)	120.5(10)	C(22)–C(23)–C(24)	120.0(12)
C(23)–C(24)–C(25)	121.3(10)	C(24)–C(25)–C(26)	118.6(10)
C(21)–C(26)–C(25)	120.8(9)	P–C(31)–C(32)	118.7(6)
P–C(31)–C(36)	123.2(7)	C(32)–C(31)–C(36)	117.7(8)
C(31)–C(32)–C(33)	120.8(8)	C(32)–C(33)–C(34)	120.4(9)
C(33)–C(34)–C(35)	119.7(9)	C(34)–C(35)–C(36)	120.5(9)
C(31)–C(36)–C(35)	120.9(9)		

A prime denotes atoms generated by the molecular two-fold symmetry axis.

the NS ligand should be a better σ donor but a worse π acceptor than NO, and that complexed NS should be more positively charged than complexed NO. This is consistent with the stretching frequencies [ν(NS) in (1) is 106 cm^{-1} *higher* than the value in the free molecule,[20] whereas ν(NO) in the corresponding NO complex is 40 cm^{-1} *lower* than in gaseous NO], and distances to the other ligands {the *trans*-Cl is 1.3 pm *further* from Os than the *cis*-Cl in (1), but the *trans*-Cl is 4.1 pm *nearer* to Ru than the *cis*-Cl in [Ru(NO)Cl$_3$(PPh$_3$)$_2$][17]}. It is less clear why the N–S distances in thionitrosyl complexes, after the necessary correction for libration, are significantly longer than in the NS molecule[21] {149.5 pm, *cf.* 150.3 (uncorrected) or 153.4 pm (corrected assuming a riding model) in (1), 155.1 (uncorrected) or 157.2 pm (corrected) in [Cr(η^5-C$_5$H$_5$)(CO)$_2$(NS)],[5] and 159.2 p.p.m. (uncorrected) in [Mo(NS)(S$_2$CNMe$_2$)$_3$][11]}. The longer NS bond and lower ν(NS) (1 180 cm^{-1}) in the Cr complex can however be attributed to greater π back-donation from Cr, which has a formal oxidation state 2 units lower than Os in (1).

Acknowledgements

We thank the Fonds der Chemischen Industrie and the Humboldt-Stiftung for support (to K. K. P.), and Dr. P. G. Jones for measuring the cell constants of (2).

References

1 H. W. Roesky and K. K. Pandey, *Adv. Inorg. Chem. Radiochem.*, 1982, **26**, 337.
2 M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Chem. Soc., Dalton Trans.*, 1979, 1.
3 M. J. Wright and W. P. Griffith, *Transition Met. Chem.*, 1982, **7**, 53.
4 B. W. S. Kolthammer and P. Legzdins, *J. Am. Chem. Soc.*, 1978, **100**, 2247.
5 T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins, and J. Trotter, *Inorg. Chem.*, 1979, **18**, 3548.
6 K. K. Pandey and U. C. Agarwala, *Z. Anorg. Allg. Chem.*, 1980, **461**, 231.
7 K. K. Pandey, K. C. Jain, and U. C. Agarwala, *Inorg. Chim. Acta*, 1981, **48**, 23.
8 K. K. Pandey and U. C. Agarwala, *Inorg. Chem.*, 1981, **20**, 1308.
9 R. Mews and C. Liu, *Angew. Chem.*, 1983, **95**, 156.
10 M. Herberhold and L. Haumaier, *Z. Naturforsch., Teil B*, 1980, **356**, 1277.
11 M. B. Hursthouse and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1979, 1362.
12 A. Oudeman, F. V. Rantwijk, and H. V. Bekkum, *J. Coord. Chem.*, 1974, **4**, 1.
13 J. R. Morton and H. W. Wilcox, *Inorg. Synth.*, 1953, **4**, 48.
14 W. G. Burns and H. J. Bernstein, *J. Chem. Phys.*, 1958, **18**, 1669.
15 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
16 K. K. Pandey, R. D. Tiwari, and U. C. Agrawala, *Indian J. Chem.*, 1981, **20**, 370.
17 B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060.
18 D. R. Salahub and R. P. Messmer, *J. Chem. Phys.*, 1976, **64**, 2039.
19 J. L. Hubbard and D. L. Lichtenberger, *Inorg. Chem.*, 1980, **19**, 1388.
20 D. Chapman, R. J. Warm, A. G. Fitzgerald, and B. D. Fyoffe, *Trans. Faraday Soc.*, 1964, **60**, 294.
21 R. F. Barrow, G. Drummond, and P. B. Zeeman, *Proc. Phys. Soc. London, Sect. A*, 1954, **67**, 365.

Received 3rd May 1983; Paper 3/705