Preparation and Crystal Structure of a Sulphinylnitrilo Complex of Rhodium(I): *trans*-$[Rh(CO)(NSO)(PPh_3)_2]$ †

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The reaction of $CsNSO_2$ with $[RhH(CO)(PPh_3)_3]$ in acetonitrile yields *trans*-$[Rh(CO)(NSO)(PPh_3)_2]$ (1) and PPh_3O. Complex (1) has been characterised by elemental analyses, i.r. spectra, and a single-crystal *X*-ray structure investigation. Crystals of (1) are triclinic, space group $P\bar{1}$, with a = 9.248(2), b = 9.502(2), c = 10.567(2) Å, α = 71.52(2), β = 89.71(2), γ = 69.80(2)°, and Z = 1. In the square-planar molecular complex the carbonyl group [Rh–C 1.843(6) Å] is in the *trans* position relative to the NSO ligand [Rh–N 1.989(9), N–S 1.48(1), S–O 1.51(1) Å; N–S–O 122.5(5)°]. The Rh–P bond lengths to the *trans*-co-ordinated phosphine ligands are 2.330(1) Å. The arrangement of the molecules in the crystal is disordered, with a superposition of two half-occupied CO and NSO ligand sites in the electron-density map, simulating the crystallographic inversion centre at the Rh site.

In recent years several papers have described synthetic and structural studies of transition-metal thionitrosyl complexes.[1] We report here the preparation of a new sulphinylnitrilo complex and for the first time the *X*-ray structure of a complex having a co-ordinated NSO^- group.

Experimental

Solvents were refluxed over P_4O_{10} or metallic sodium and freshly distilled. All reactions were carried out under dry nitrogen. I.r. spectra were recorded on a Perkin-Elmer 735B spectrophotometer with Nujol mulls. $CsNSO_2$[2] and $[RhH(CO)(PPh_3)_3]$[3] were prepared as described in the literature.

trans-*Carbonyl(sulphinylnitrilo)bis(triphenylphosphine)-rhodium*(I), (1).—A solution of $CsNSO_2$ (0.22 g, 1 mmol) in acetonitrile (100 cm^3) was added with stirring to a solution of $[RhH(CO)(PPh_3)_3]$ (0.92 g, 1 mmol) in acetonitrile (30 cm^3) under a nitrogen atmosphere at room temperature. The reaction mixture was refluxed for 4 h and then filtered. The filtrate was concentrated under vacuum to 25 cm^3. On cooling the filtrate, yellow crystals were formed which were recovered by filtration. The crystals were washed twice with acetonitrile (15 cm^3) and dried under a nitrogen atmosphere. Yield, 0.4 g (56%) (Found: C, 61.8; H, 4.0; N, 2.1; S, 4.7. Calc. for $C_{37}H_{30}NO_2P_2RhS$: C, 61.9; H, 4.20; N, 1.95; S, 4.45%). I.r.: 3 060m, 2 965m, 1 985s, 1 480s, 1 435s, 1 240s, 1 190m, 1 160m, 1 100s, 1 050s, 1 040m, 1 000m, 750s, 710s, 690s, 580s, 530s, and 510s cm^{-1}.

Crystal Data.—$C_{37}H_{30}NO_2P_2RhS$, M = 717.57, triclinic, space group $P\bar{1}$, a = 9.248(2), b = 9.502(2), c = 10.567(2) Å, α = 71.52(2), β = 89.71(2), γ = 69.80(2)°, U = 820.8 Å^3, D_m = 1.43(1), Z = 1, D_c = 1.427 g cm^{-3}, $F(000)$ = 366, μ(Mo-K_α) = 6.9 cm^{-1}.

Crystal Structure Analysis.—The unit-cell dimensions of the triclinic crystals were obtained by least-squares refinement from diffractometer co-ordinates of 20 high-angle reflections. For the structure analysis a room-temperature data set of 3 605 single-crystal reflection intensities was measured up to $(\sin\theta)/\lambda$ = 0.64 Å^{-1} with Mo-K_α radiation (λ = 0.710 69 Å) on a Syntex $P2_1$ four-circle diffractometer, using a graphite monochromator and a scintillation counter (2θ—θ scan mode, scan speed 3—30° min^{-1} according to intensity, crystal size 0.24 × 0.18 × 0.16 mm). 3 377 data with $I > 1.96\sigma(I)$ were considered as observed and were used in the calculations. The variance of I was calculated as $\sigma^2(I) = S + (B_1 + B_2)(t_S/2t_B)^2$, where S, B_1, and B_2 are the scan and individual background counts, and where t_S and t_B are the counting times ($t_B = t_S/2$ was used).

The structure was solved in the space group $P\bar{1}$ (which was suggested by the statistical distribution of the normalized structure factors) from the three-dimensional Patterson function and by subsequent Fourier syntheses. After least-squares refinement of the Rh and triphenylphosphine atoms, the CO and NSO ligand atoms were obtained from a ΔF synthesis as a superposition of two half-occupied disordered positions related by the crystallographic centre of inversion at the Rh site. At this stage an attempt was made to reduce the crystal symmetry to $P1$, which, however, did not lead to a successful refinement. In the disordered structure the slight disturbance in the crystal packing induced by the slightly different space requirements of the NSO and CO ligands can be recognised in the elevated thermal parameters of the neighbouring phenyl ring, C(13)—C(18). The experimental electron density in the region of the superposed disordered CO and NSO ligands is shown in Figure 1.

Anisotropic refinement in space group $P\bar{1}$ (isotropic thermal parameters for atoms of the disordered NSO and CO ligands to avoid correlation) with fixed calculated H-atom co-ordinates (B = 7 Å^2) included in the structure factor calculations yielded final values of $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ = 0.047 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ = 0.045. The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $1/w = \sigma^2(F_o) + (0.005F_o)^2$ and $\sigma(F_o) = \sigma(I)/(2F_oL_p)$; L_p = Lorentz polarisation correction. Scattering factors for neutral Rh (corrected for anomalous dispersion), S, P, N, C, and H were taken from International Tables.[4] Final atomic co-ordinates are given in Table 1.

Results and Discussion

$CsNSO_2$ reacts with $[RhH(CO)(PPh_3)_3]$ to yield *trans*-$[Rh(CO)(NSO)(PPh_3)_2]$ (1) and triphenylphosphine oxide,

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† *trans*-Carbonyl(sulphinylnitrilo)bis(triphenylphosphine)rhodium-(I).

Supplementary data available (No. SUP 56010, 21 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic co-ordinates with standard deviations for *trans*- [Rh(CO)(NSO)(PPh$_3$)$_2$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0	0	0	C(7)	−0.117 4(4)	0.791 0(4)	0.241 4(4)
S	−0.278 27(24)	0.264 22(30)	0.074 44(21)	C(8)	−0.214 9(5)	0.759 8(5)	0.371 7(4)
O(1)	−0.178 0(8)	0.329 6(8)	0.133 1(7)	C(9)	−0.363 1(5)	0.759 3(5)	0.398 7(4)
O(2)	−0.284 6(8)	0.186 5(7)	0.091 0(6)	C(10)	−0.471 1(5)	0.787 0(5)	0.296 4(5)
N	−0.212 9(12)	0.136 4(11)	0.015 9(10)	C(11)	−0.435 2(5)	0.817 2(6)	0.167 4(5)
C(19)	−0.170 6(6)	0.124 1(6)	0.056 8(5)	C(12)	−0.288 6(5)	0.821 2(6)	0.139 2(4)
P	0.012 26(11)	0.795 04(10)	0.197 34(10)	C(13)	0.120 7(5)	0.593 0(4)	0.200 4(4)
C(1)	0.104 9(4)	0.808 9(4)	0.341 9(4)	C(14)	0.281 8(6)	0.541 0(5)	0.209 8(5)
C(2)	0.112 7(5)	0.955 0(5)	0.333 9(4)	C(15)	0.368 6(7)	0.392 6(6)	0.202 6(6)
C(3)	0.182 6(5)	0.970 4(5)	0.442 2(5)	C(16)	0.296 7(9)	0.297 0(6)	0.182 0(5)
C(4)	0.243 6(5)	0.843 3(6)	0.559 0(5)	C(17)	0.139 0(9)	0.349 7(6)	0.167 6(5)
C(5)	0.236 5(5)	0.697 3(6)	0.568 6(5)	C(18)	0.048 4(6)	0.496 9(5)	0.178 0(4)
C(6)	0.167 3(5)	0.680 5(5)	0.459 4(5)				

Table 2. Bond distances (Å) and angles (°) with standard deviations for *trans*-[Rh(CO)(NSO)(PPh$_3$)$_2$]

Rh–P	2.330(1)	P–C(7)	1.823(4)	C(6)–C(1)	1.387(6)	C(13)–C(14)	1.391(8)
Rh–N	1.989(9)	P–C(13)	1.823(4)	C(7)–C(8)	1.382(6)	C(14)–C(15)	1.387(9)
Rh–C(19)	1.843(6)	C(1)–C(2)	1.391(6)	C(8)–C(9)	1.400(7)	C(15)–C(16)	1.363(9)
N–S	1.480(12)	C(2)–C(3)	1.388(7)	C(9)–C(10)	1.372(7)	C(16)–C(17)	1.361(12)
S–O(1)	1.509(10)	C(3)–C(4)	1.376(7)	C(10)–C(11)	1.365(7)	C(17)–C(18)	1.399(8)
C(19)–O(2)	1.137(10)	C(4)–C(5)	1.383(8)	C(11)–C(12)	1.397(8)	C(18)–C(13)	1.378(7)
P–C(1)	1.818(4)	C(5)–C(6)	1.400(7)	C(12)–C(7)	1.384(6)		

P–Rh–N	93.6(2)	Rh–P–C(13)	116.5(1)	C(4)–C(5)–C(6)	119.7(4)	C(11)–C(12)–C(7)	120.6(4)
P′–Rh–N	86.4(2)	C(1)–P–C(7)	105.8(2)	C(5)–C(6)–C(1)	120.7(4)	P–C(13)–C(14)	118.8(3)
P–Rh–C(19)	86.3(2)	C(1)–P–C(13)	103.7(2)	P–C(7)–C(8)	122.9(3)	P–C(13)–C(18)	122.1(3)
P′–Rh–C(19)	93.7(2)	C(7)–P–C(13)	104.0(2)	P–C(7)–C(12)	118.2(3)	C(18)–C(13)–C(14)	118.6(4)
N–Rh–C(19)	164.4(3)	P–C(1)–C(2)	118.3(3)	C(12)–C(7)–C(8)	118.9(4)	C(13)–C(14)–C(15)	120.9(5)
Rh–N–S	135.1(8)	P–C(1)–C(6)	122.8(3)	C(7)–C(8)–C(9)	120.1(4)	C(14)–C(15)–C(16)	120.3(6)
N–S–O(1)	122.5(5)	C(6)–C(1)–C(2)	118.9(4)	C(8)–C(9)–C(10)	120.3(4)	C(15)–C(16)–C(17)	119.1(6)
Rh–C(19)–O(2)	170.8(7)	C(1)–C(2)–C(3)	120.0(4)	C(9)–C(10)–C(11)	120.1(5)	C(16)–C(17)–C(18)	121.9(6)
Rh–P–C(1)	112.3(1)	C(2)–C(3)–C(4)	121.1(5)	C(10)–C(11)–C(12)	120.0(5)	C(17)–C(18)–C(13)	119.1(5)
Rh–P–C(7)	113.5(1)	C(3)–C(4)–C(5)	119.6(4)				

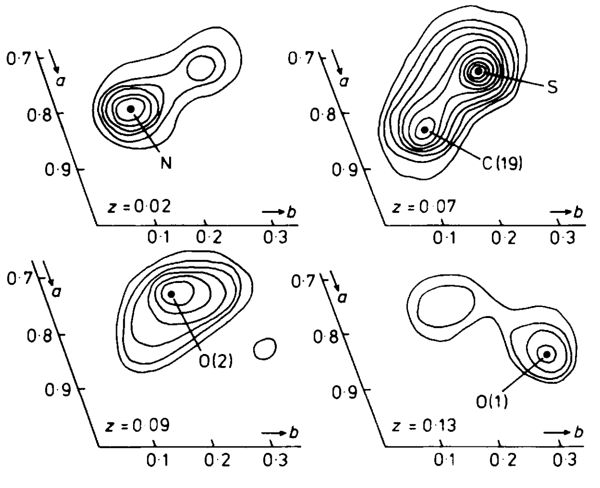

Figure 1. Electron density in the region of the superposed disordered CO and NSO ligands. Contours are in steps of 0.6 e Å^{-3} starting with +0.6 e Å^{-3}. Sections are parallel to (001); values given are in fractions of the unit-cell edges

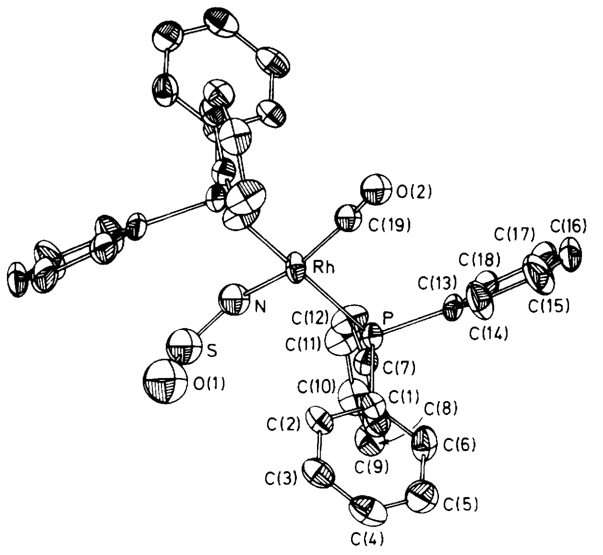

Figure 2. Molecular structure of *trans*-[Rh(CO)(NSO)(PPh$_3$)$_2$] in the crystal with atom numbering (50% probability thermal ellipsoids)

equation (i). Complex (1) is a yellow crystalline solid that melts

$$[RhH(CO)(PPh_3)_3] + CsNSO_2 \longrightarrow [Rh(CO)(NSO)(PPh_3)_2] + PPh_3O + CsH \quad (i)$$

at 190 °C with decomposition. In the i.r. spectrum bands at 1 985, 1 240, 1 050, and 580 cm^{-1} were observed besides the characteristic bands of triphenylphosphine. The band at 1 985 cm^{-1} is assigned to ν(CO), indicating that oxidation of the rhodium(I) of the starting material (1 918 cm^{-1}) has not occurred. The absorption bands at 1 240, 1 050, and 580

cm^{-1} are tentatively assigned to ν_{asym}(NSO), ν_{sym}(NSO), and δ(NSO), respectively.

The crystal structure contains an arrangement of mononuclear square-planar molecules with a *trans* configuration of the triphenylphosphine ligands. A view of the complex molecule is presented in Figure 2; the bond distances and angles are given in Table 2.

The interesting novel NSO ligand shows bond lengths which can be considered close to double bonds. The Rh–N distance (1.989 Å) is significantly longer than the Rh–C value (1.843 Å) in the *trans* position, indicating an absence of bond strengthening by back bonding. The N–S–O bond angle in the ligand (122.5°) is consistent with the double-bond valence structure, whereas the relatively large Rh–N–S bond angle (135.1°) is probably influenced by interligand and intermolecular repulsion forces. The Rh–P bond lengths (2.330 Å) are in the region expected for triphenylphosphine ligands in *trans* positions to each other as exemplified by values of 2.338(4) Å in $[Rh(H)Cl(SiCl_3)(PPh_3)_2]$,[5] 2.290(4) Å in *trans*-$[Rh\{N{=}C(CF_3)_2\}\{C[NMe(CH_2)_2NMe]\}(PPh_3)_2]$,[6] 2.367(1) Å in $[RhCl_2(NO)(PPh_3)_2]$,[7] and 2.378(2) Å in $[RhCl(PhCONCS)_2(PPh_3)_2]$.[8] As the bond lengths and angles in Table 2 show, the internal structures of the CO and phosphine ligands are normal. As indicated in the Experimental section, the disorder of the molecules by a statistical interchange of the CO and NSO ligands across the false centre of inversion at the Rh site imposes a slight disturbance of the crystal packing because of the somewhat different space requirements of CO and NSO. This intermolecular stress may also be responsible for the significant deviation of the quasi-tetragonal coordination of Rh from planarity: N deviates by as much as 0.47 Å from the plane defined by Rh, P, P′, and C(19).

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