METAL-ORGANIC COMPOUNDS

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mer,cis-Chlorotris(dimethylphenylphosphine)nitrido(trifluoromethylsulfonato)rhenium(V)

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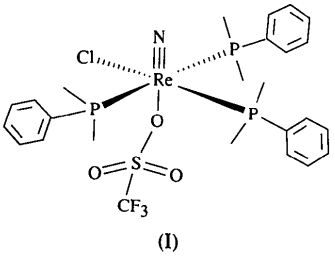
Abstract

The title compound, [ReNCl(CF_3SO_3)($C_8H_{11}P$)$_3$], is formed by the reaction of [ReNCl$_2$($C_8H_{11}P$)$_3$] with excess trifluoromethanesulfonic acid. The phosphine ligands are coordinated meridionally. The trifluoromethanesulfonate ligand is in a *trans* position with respect to the terminal nitrido N atom with an exceptionally long Re—O bond length of 2.403 (5) Å, which is the result of the strong structural *trans* influence of 'N^{3-}'.

Comment

Terminal nitrido ligands are known as strong π donors which cause a considerable structural *trans* influence. As part of our systematic work on the reactivity and structure of rhenium–nitrido complexes (Abram & Ritter, 1993, 1994; Ritter & Abram, 1994), we studied the reaction of [ReNCl$_2$(Me$_2$PhP)$_3$] with trifluoromethanesulfonic acid (2 h reflux in CH_2Cl_2), which results in the formation of air-stable brownish yellow crystals of [ReNCl(OSO_2CF_3)(Me$_2$PhP)$_3$], (I). The compound was obtained in 85% yield and was recrystallized from CH_2Cl_2/*n*-hexane solution.



(I)

The complex was characterized by elemental analysis and spectroscopic methods. An intense band in the IR spectrum at 1050 cm^{-1} can be assigned to the rhenium–nitrogen triple bond. FAB-MS studies confirmed the coordination of trifluoromethanesulfonate, showing the molecular ion peak at *m*/*z* = 799. Fragmentation mainly occurs by the cleavage of metal–ligand bonds, as can be concluded from the intense fragment peaks at *m*/*z* = 650 {[ReNCl(Me$_2$PhP)$_3$]} and 512 {[ReNCl(Me$_2$PhP)$_2$]}. ^{1}H and ^{13}C NMR spectra are well resolved and characterized by narrow lines. They provide evidence for the diamagnetism of the d^2 rhenium(V) complex. The proton spectrum showed a coupling pattern typical of three meridionally coordinated phosphine ligands (Abram, Lorenz, Kaden & Scheller, 1988).

The Re atom in [ReNCl(OSO_2CF_3)(Me$_2$PhP)$_3$] is coordinated in a distorted octahedral manner (Fig. 1). Atoms Re, P1, P2 and P3 are coplanar within 0.056 (1) Å, whereas the Cl atom deviates from this least-squares plane by 0.717 (4) Å. This distortion is also evident from the N—Re—Cl angle of 106.0 (2)°. The short Re—N distance of 1.642 (6) Å is characteristic of terminal nitrido ligands and corresponds well with values found in similar complexes (Abram & Ritter, 1993, 1994; Ritter & Abram, 1994). The 'N^{3-}' ligand is the source of a strong structural *trans* influence which weakens the Re—O1 bond. An exceptionally long Re—O1 distance of 2.403 (5) Å was detected. In accordance with the *trans* influence of Me$_2$PhP, the Re—P1 and Re—P2 bond lengths are appreciably longer than the Re—P3 distance.

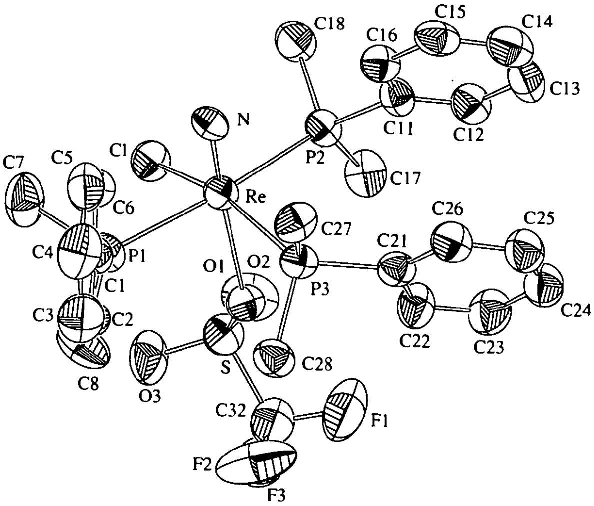


Fig. 1. *ORTEP* (Johnson, 1965) diagram of the title complex showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Crystal data

[ReNCl(CF_3SO_3)($C_8H_{11}P$)$_3$]
M_r = 799.14

Mo *Kα* radiation
λ = 0.7107 Å

Monoclinic
$P2_1/c$
$a = 17.589(3)$ Å
$b = 10.164(1)$ Å
$c = 16.807(4)$ Å
$\beta = 84.16(1)°$
$V = 2989.2(9)$ Å^3
$Z = 4$
$D_x = 1.776$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 8.3–13.6°$
$\mu = 4.432$ mm^{-1}
$T = 213(2)$ K
Block
0.4 × 0.2 × 0.2 mm
Brownish yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
7366 measured reflections
6380 independent reflections
4784 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0534$

$\theta_{\rm max} = 26.81°$
$h = -22 \rightarrow 22$
$k = -1 \rightarrow 12$
$l = -21 \rightarrow 0$
3 standard reflections monitored every 200 reflections frequency: 60 min intensity decay: 2.1%

Refinement

Refinement on F^2
$R(F) = 0.0513$
$wR(F^2) = 0.1469$
$S = 1.097$
6377 reflections
344 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 7.0155P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 1.753$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.793$ e Å^{-3}
Extinction correction: $F_c^* = 1/kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{1/4}$
Extinction coefficient: $\chi = 0.0049(4)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Re	0.19487 (2)	0.05854 (3)	0.49270 (2)	0.04047 (15)
Cl	0.17837 (13)	0.0587 (2)	0.63762 (12)	0.0526 (5)
S	0.33735 (13)	0.2490 (2)	0.58366 (13)	0.0539 (5)
P1	0.11622 (14)	0.2600 (2)	0.50289 (13)	0.0497 (5)
P2	0.27004 (13)	−0.1431 (2)	0.50604 (12)	0.0441 (5)
P3	0.24768 (13)	0.1026 (2)	0.35612 (12)	0.0428 (5)
N	0.1236 (4)	−0.0279 (6)	0.4643 (4)	0.0429 (15)
O1	0.3035 (3)	0.1914 (6)	0.5157 (3)	0.0476 (13)
O2	0.3696 (5)	0.1585 (8)	0.6353 (4)	0.079 (2)
O3	0.2935 (4)	0.3517 (8)	0.6233 (4)	0.079 (2)
F1	0.4657 (4)	0.2518 (9)	0.4939 (5)	0.113 (3)
F2	0.4573 (4)	0.3984 (7)	0.5842 (4)	0.093 (2)
F3	0.3980 (5)	0.4205 (9)	0.4818 (6)	0.130 (4)
C1	0.0610 (5)	0.2875 (8)	0.4188 (5)	0.046 (2)
C2	0.0687 (6)	0.3978 (10)	0.3704 (6)	0.058 (2)
C3	0.0252 (7)	0.4134 (12)	0.3070 (7)	0.076 (3)
C4	−0.0269 (6)	0.3197 (13)	0.2917 (6)	0.074 (3)
C5	−0.0354 (5)	0.2110 (11)	0.3396 (6)	0.065 (3)
C6	0.0085 (5)	0.1929 (9)	0.4016 (6)	0.055 (2)
C7	0.0414 (6)	0.2507 (12)	0.5849 (6)	0.073 (3)
C8	0.1603 (7)	0.4168 (9)	0.5187 (8)	0.076 (3)
C11	0.2815 (5)	−0.2491 (8)	0.4187 (5)	0.046 (2)
C12	0.3506 (5)	−0.3084 (9)	0.3932 (5)	0.055 (2)
C13	0.3574 (7)	−0.3896 (10)	0.3273 (6)	0.065 (3)
C14	0.2968 (7)	−0.4150 (9)	0.2857 (6)	0.067 (3)
C15	0.2271 (6)	−0.3585 (9)	0.3104 (5)	0.057 (2)
C16	0.2191 (5)	−0.2742 (8)	0.3763 (5)	0.049 (2)
C17	0.3632 (5)	−0.1243 (11)	0.5406 (6)	0.060 (2)
C18	0.2244 (6)	−0.2552 (9)	0.5797 (5)	0.060 (2)
C21	0.3365 (5)	0.0216 (8)	0.3187 (5)	0.045 (2)
C22	0.4008 (5)	0.0498 (9)	0.3555 (6)	0.058 (2)
C23	0.4693 (6)	−0.0106 (11)	0.3300 (7)	0.068 (3)
C24	0.4753 (6)	−0.0941 (10)	0.2672 (6)	0.064 (3)
C25	0.4116 (6)	−0.1184 (10)	0.2274 (6)	0.063 (2)
C26	0.3429 (6)	−0.0629 (9)	0.2537 (5)	0.055 (2)
C27	0.1813 (5)	0.0604 (9)	0.2859 (5)	0.054 (2)
C28	0.2707 (6)	0.2739 (8)	0.3338 (5)	0.056 (2)
C30	0.4176 (6)	0.3355 (12)	0.5332 (7)	0.071 (3)

Table 2. *Selected geometric parameters* (Å, °)

Re—N	1.642 (6)	Re—P1	2.467 (2)
Re—O1	2.403 (5)	S—O2	1.421 (7)
Re—Cl	2.423 (2)	S—O3	1.422 (7)
Re—P3	2.429 (2)	S—O1	1.464 (5)
Re—P2	2.461 (2)	S—C30	1.800 (11)
N—Re—O1	172.3 (3)	Cl—Re—P2	85.37 (7)
N—Re—Cl	106.0 (2)	P3—Re—P2	94.72 (7)
O1—Re—Cl	81.61 (13)	N—Re—P1	91.4 (2)
N—Re—P3	93.1 (2)	O1—Re—P1	88.39 (15)
O1—Re—P3	79.29 (13)	Cl—Re—P1	85.46 (7)
Cl—Re—P3	160.91 (8)	P3—Re—P1	94.03 (8)
N—Re—P2	90.8 (2)	P2—Re—P1	170.83 (7)
O1—Re—P2	90.57 (15)	S—O1—Re	138.0 (3)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*89 (Keller, 1989) and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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