ELSEVIER

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 314 (2001) 37–41

Inorganica Chimica Acta

Synthesis of neutral rhenium(V) complexes with fluorinated benzenethiols: the crystal and molecular structure of $[ReO(C_6H_4S\text{-}2\text{-}F)_3(PPh_3)]$

David Morales-Morales [a], Yifan Zheng [a], Jonathan R. Dilworth [a,*1], Rocío Redón [b], Hugo Torrens [b,*2]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*
[b] *DEPg, Facultad de Química, UNAM, Cd. Universitaria, 04510 Mexico City, Mexico*

Received 9 August 2000; accepted 6 November 2000

Abstract

The complexes $[ReO(SR_f)_3(PPh_3)]$ and $[ReN(SR_f)_2(PPh_3)_2]$ [$R_f = C_6F_5$ (**1**) and (**6**), C_6F_4-4-H (**2**) and (**7**), C_6H_4-2-F (**3**) and (**8**), C_6H_4-3-F (**4**) and (**9**) and C_6H_4-4-F (**5**) and (**10**)] were synthesized in good yields by reacting $[ReOCl_3(PPh_3)_2]$ or $[ReNCl_2(PPh_3)_2]$ and the lead salt of the corresponding fluorobenzenethiol $[Pb(SR_f)_2]$. In contrast, when the free thiol HSC_6F_5 was employed in the presence of NEt_3 as base, the ionic species $[ReO(SC_6F_5)_4][NEt_3 \cdot HCl]$ (**11**) was isolated. The X-ray crystal structure of **3** was determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhenium complexes; Fluorinated thiols; Oxo complexes; Thiolate complexes; Nitrido complexes

1. Introduction

The chemistry of aromatic sterically hindered thiols has been studied extensively in recent years owing to the importance that some of its complexes may play as models for active sites in metalloproteins [1]. This is particularly true in the case of nitrogenase, thought to be the key catalyst in the reduction of dinitrogen to ammonia [2]. Among the sterically hindered thiolate ligands, fluorinated benzenethiols have occupied an important place, owing to their ability to stabilize unusual geometries, oxidation states and intra- or inter-molecular interactions [3]. Some complexes have also been used as highly active catalysts in hydroformylation and polymerization reactions [4] and identified as active intermediates in desulfurization processes [5]. The success of the fluorinated thiols over other sterically hindered thiols lies in the facility with which steric and electronic properties can be tuned by changing fluorine substitution or by increasing the number of fluorine atoms in the aromatic ring [6]. In recent years the synthesis and reactivity of rhenium complexes with sterically hindered thiols have been studied, and although the complexes are potentially capable of binding small molecules, this ability is a sensitive function of the nature of the substituents of the thiolate ligand [1]. The usual product of reaction of Re(V) precursors with thiolate anions is $[ReO(SR)_4]^-$ and neutral rhenium thiolate complexes, such as $[ReO(SR)_3(PR_3)]$, are very rare, and represented by the single reported example $[ReO(DMT)_3(PR_3)]$ (DMT = 2,6-dimethylbenzenethiolate). This complex was obtained by reacting trimethylsilyl-2,6-dimethylbenzenethiolate (Me_3SiDMT) with $[ReOCl_3(PPh_3)_2]$ or $[ReH_7(PPh_3)_2]$ with RSSR (SR = DMT) [7]. Rhenium nitrido complexes with aromatic thiolate ligands are also relatively uncommon; however, the Re(VI) complex $[ReN(TIPT)_4]^-$ was obtained when the sodium salt of TIPTH (2,4,6-triisopropylbenzenethiol) was reacted with $[ReNCl_2(PPh_3)_2]$ [8]. In an effort to effect an efficient synthesis of complexes with the formulation $[ReO(SR)_3(PR_3)]$ and $[ReN(SR)_2(PR_3)_2]$ we have attempted the metathetical

---

[1] *Corresponding author. Tel.: +44-1865-272 639; fax: +44-1865-272 690; e-mail: jon.dilworth@chem.ox.ac.uk

[2] *Corresponding author.

PII: S0020-1693(00)00378-9

reactions of fluorobenzenethiolate lead salts with $[ReOCl_3(PPh_3)_2]$ or $[ReNCl_2(PPh_3)_2]$.

2. Experimental

2.1. Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, and solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. IR spectra were recorded on a Perkin–Elmer Paragon FT-IR spectrometer as Nujol mulls and ^1H (400.03 MHz), ^{19}F (376.41 MHz) and ^{31}P NMR (161.94 MHz) spectra on a JEOL EX270 spectrometer in $CDCl_3$ solutions. Elemental analyses were determined on a Perkin–Elmer 240 at the University of Essex. The fluorinated benzenethiols were obtained from Aldrich Chemical Co. and used without further purification. The starting materials $[Pb(SR_f)_2]$ $[R_f = C_6F_5$, C_6F_4-4-H, C_6H_4-2-F, C_6H_4-3-F and C_6H_4-4-F] [9], $[ReOCl_3(PPh_3)_2]$ [10] and $[ReNCl_2(PPh_3)_2]$ [11] were prepared according to published procedures.

2.2. Synthesis of *$[ReO(SR_f)_3(PPh_3)]/[ReN(SR_f)_2(PPh_3)_2]$*

To a dichloromethane solution of $[ReOCl_3(PPh_3)_2]$ (50 mg, 0.060 mmol) or $[ReNCl_2(PPh_3)_2]$ (50 mg, 0.063 mmol) equivalent amounts of the lead salts were added. The resulting suspensions were stirred for 24 h at room temperature. After this time the resulting solutions were filtered through a short plug of Celite and the solvent removed under vacuum. For the reactions with $Pb(SR_f)_2$ $R_f = C_6H_4$-2-F, C_6H_4-3-F, C_6H_4-4-F, further purification was required and column chromatography was performed using silica-gel as stationary phase and CH_2Cl_2 as eluent first and then pentane. Dark-green fractions were collected and the solvent evaporated under vacuum. A second fraction (brown–reddish) was separated; however, the amounts obtained were too small to carry out any further analysis.

2.3. Single crystal X-ray structure determination of *$[ReO(C_6H_4S\text{-}2\text{-}F)_3(PPh_3)]$ (**3**)*

Intensity data were collected on an Enraf–Nonius CAD4 diffractometer [12] with monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centered reflections in the range $1.52 < \theta < 25°$. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 2 h of exposure. No loss of intensity was observed. Three standard reflections were measured every 200 reflections to check the crystal orientation. The data were corrected for Lorentz and polarization factors and an absorption correction was applied using ψ-scans of nine reflections. The structure was solved via direct methods [13] and refined by F_o^2 by full-matrix least squares [14]. All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in idealized positions with U_{iso} free to refine. The weighting scheme gave satisfactory agreement analyses. Final R indices $[5272 I > 2\sigma(I)]$ $R_1 = 0.0271$ (on F), $wR_2 = 0.0707$. The largest difference peak and hole were 1.485 e^- Å^{-3} and -0.397 e^- Å^{-3} respectively; the highest peak in the final difference Fourier map was in the vicinity of the metal atoms; the final map had no significant features. The maximum shift/e.s.d. value was 0.002. Sources of scattering factors were as in Ref. [14]. The details of the structure determination are given in Table 1; selected bond lengths and angles are in Table 2. The numbering of the atoms is shown in Fig. 1 (ZORTEP) [15].

3. Results and discussion

3.1. Synthesis of the complexes *$[ReO(SR_f)_3(PPh_3)]$ and $[ReN(SR_f)_2(PPh_3)_2]$*

The reaction of the starting materials $[ReOCl_3(PPh_3)_2]$ or $[ReNCl_2(PPh_3)_2]$ with the lead salts of the fluorobenzenethiols in CH_2Cl_2 affords the thiolate complexes $[ReO(SR_f)_3(PPh_3)_2]$ and $[ReN(SR_f)_2(PPh_3)_2]$ in good yields (Schemes 1 and 2). The reactions proceed cleanly to yield only the desired species, except in the cases of $R_f = C_6H_4$-2-F (**3**) and (**8**), C_6H_4-3-F (**4**) and (**9**), C_6H_4-4-F (**5**) and (**10**) where further purification was necessary. All complexes are stable in the solid state, but tend to decompose in solution under aerobic conditions; the products of decomposition were not identified. The results obtained contrast with those of other reactions carried out using free thiophenol or other sterically hindered thiols in the presence of base which give exclusively ionic species with the formulation $[ReX(SR)_4]^-$, X = O, N [16,17]. The use of the essentially covalent lead salts avoids the use of thiolate anion and permits the stoichiometric, non-reductive introduction of thiolate ligands. The differences in products formed is probably a kinetic effect originating from the necessity to form a four-center transition state prior to elimination of lead chloride. This is almost certainly slower than simple nucleophilic attack of thiolate anion. The proposed formulations were confirmed by elemental analyses, IR spectroscopy, mass spectrometry and multinuclear NMR data (Table 1). The infrared spectroscopic data obtained show intense bands for all the oxo complexes in the range 918 to

940 cm^{-1}, which are typical for the Re=O stretching vibration. The ^{1}H NMR spectrum of the complexes is not very revealing, and only the signals corresponding to the aromatic protons in the PPh$_3$ and the thiolate ligands are observed. The ^{31}P NMR exhibits a singlet in all cases to confirm the proposed structures, with a single phosphine ligand for the oxo complexes or, in the case of the nitrido species, two equivalent phosphorus groups probably in a trans arrangement. The ^{19}F NMR shows the signals expected for the fluorine atoms present in the corresponding fluorobenzene thiolates [18]. Elemental analysis and mass spectrometry experiments also confirm the proposed formulations for the complexes as monomeric species.

Table 1
Crystal data and structure refinement [ReO(SC$_6$H$_4$-2-F)$_3$(PPh$_3$)] (**3**)

Empirical formula	$C_{36}H_{27}F_3OPReS_3$
Formula weight	845.93
Temperature (K)	293(2)
Diffractometer	Enraf–Nonius CAD4
Wavelength (Å)	0.710 73
Collection method	ω–2θ
Scan rate (min^{-1})	1–7 (in ω)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.7545(10)
b (Å)	12.174(2)
c (Å)	14.766(2)
α (°)	71.405(10)
β (°)	71.142(10)
γ (°)	81.992(10)
V (Å^3)	1732.6(4)
Z	2
No. of reflections (lattice)	25
θ range (lattice)	15–16
D_{calc} (g cm^{-3})	1.621
Absorption coefficient (mm^{-1})	
$F(000)$	832
Crystal size (mm^3)	0.55 × 0.3 × 0.25
θ range for data collection (°)	1.52 to 25.02
Index ranges	$-12 \leq h \leq 0$, $-14 \leq k \leq 14$, $-17 \leq l \leq 16$
Reflections collected	6122
Independent reflections	6104 ($R_{int} = 0.0104$)
Absorption correction	ψ-scan
Max. and min. transmission	1, 89.9
Standard decay correction	0
Program used	SHELXL-93 [14]
Solution method (direct)	SHELXS-86 (Sheldrick, 1991)
Weighting scheme	calc $w = 1/[\sigma^2(F_o^2) + (0.046\,69P)$ $2 + 0.6071P]$ where $P = (F_o^2 + 2F_c^2)/3$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6104/0/406
Goodness-of-fit on F^2	1.103[a]
R indices [5272$I > 2\sigma(I)$]	$R_1 = 0.0271$, $wR_2 = 0.0707$[b]
R indices (all data)	$R_1 = 0.0379$, $wR_2 = 0.0743$[b]
Largest diff. peak and hole (e$^-$ Å^{-3})	1.485 and −0.397
Max. shift/e.s.d.	0.002

[a] $S = [w(F_o)^2 - (F_c)^2)^2/(n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters.

[b] $R_1 = |F_o - F_c|/|F_o|$, $wR_2 = [w((F_o)^2 - (F_c)^2)^2/w(F_o)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for [ReO(SC$_6$H$_4$-2-F)$_3$(PPh$_3$)] (**3**)

Bond lengths (Å)		Bond angles (°)	
Re–O	1.6893(3)	O–Re–S(3)	114.92(13)
Re–S(3)	2.2866(12)	O–Re–S(2)	118.54(12)
Re–S(2)	2.3071(11)	S(3)–Re–S(2)	123.88(5)
Re–S(1)	2.3157(11)	S(1)–Re–P	162.68(4)
Re–P	2.5093(11)	O–Re–S(1)	104.91(12)
		S(3)–Re–S(1)	86.94(4)
		S(2)–Re–S(1)	94.85(4)
		O–Re–P	92.02(12)
		S(3)–Re–P	86.53(4)
		S(2)–Re–P	79.87(4)

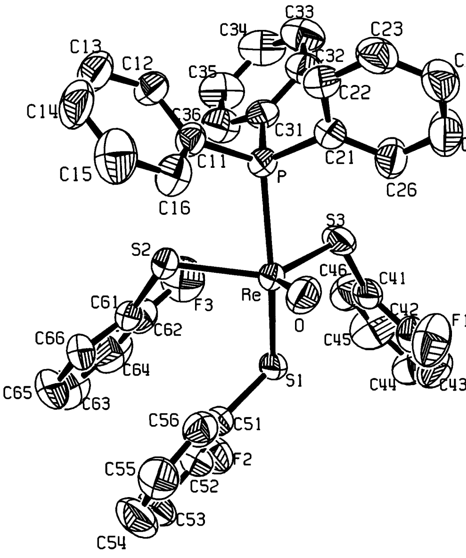
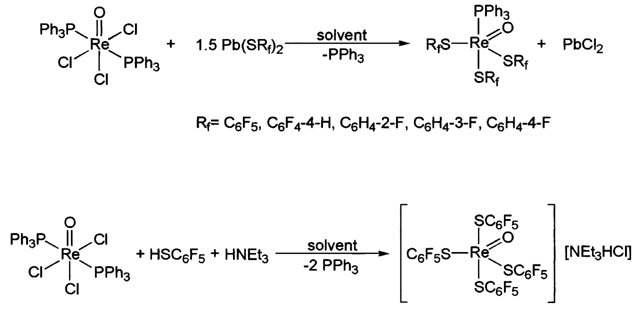
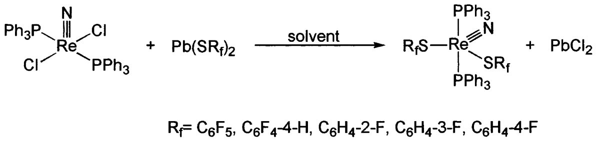


Fig. 1. A ZORTEP representation of the structure [ReO(SC$_6$H$_4$-2-F)$_3$(PPh$_3$)] (**3**) at 50% probability, showing the atom-labeling scheme.



Scheme 1. Preparation of oxo-complexes of rhenium(V) with fluorobenzenethiolates.



Scheme 2. Preparation of nitrido-complexes of rhenium(V) with fluorobenzenethiolates.

3.2. The X-ray crystal structure of *$[ReO(SC_6H_4\text{-}2\text{-}F)_3(PPh_3)]$* (**3**)

The details of the structure determination of complex **3** are given in Table 1. The ZORTEP representation of the structure is given in Fig. 1, together with the atom-labeling scheme. Selected bond lengths and angles are given in Table 2. The overall geometry about the Re atom is best described as being distorted trigonal bipyramidal (tbp), with the equatorial plane comprising the oxo atom and two thiolate ligands and the third thiolate and triphenylphosphine occupying the apical sites. The equatorial ligands and P–C bonds of PPh_3 are staggered with torsion angles of average 157.6° [S(3)–Re–P–C(11) = 163.1, S(2)–Re–P–C(21) = 154.4, O–Re–P–C(31) = 155.3] to minimize steric interactions. The aryl groups of the equatorial thiolates are disposed to the side of the equatorial plane away from the bulky triphenylphosphine ligand. The Re=O distance is very similar to that of the analogous species $[ReO(DMT)_3(PPh_3)]$ [1.694(6) Å] [7] and the anionic complex $[ReO(DIPT)_4][Ph_3PSC_6H_3{}^iPr_2]$ [1.70(2) Å] [17]. The Re–P distance [2.5093(11) Å] is similar to those observed in $[ReO(DMT)_3(PPh_3)]$ [2.521(2) Å] and $[Re(DMT)_3(PPh_3)(PHPh_2)]$ [2.455(4) Å] [7]. The Re–S distances [Re–S(3) 2.2866(12) Å, Re–S(2) 2.3071(11) Å, Re–S(1) 2.3157(11) Å] are very similar and also comparable to those observed in $[ReO(DMT)_3(PPh_3)]$ [Re–S(3) 2.301(2) Å, Re–S(2) 2.293(2) Å, Re–S(1) 2.319(2) Å] [7]. Based on these results, and those obtained from the spectroscopic techniques, we can conclude that the other oxo complexes should exhibit the same tbp structure in the solid state. In the absence of an X-ray crystal structure for the nitrido compounds, and according to the analytical and spectroscopic data, it is very likely that these series of complexes have a geometry similar to that observed for the $[ReO(SR)_4]^-$ species [16,17]. These have a square pyramidal geometry, and in the case of the complexes described here the phosphines will presumably be located at the base of the pyramid in a trans arrangement. The two thiolates complete the basal plane, and the nitride ligand is located in the apical position.

4. Conclusions

A series of neutral oxo and nitrido Re(V) complexes with fluorinated benzenethiols has been synthesized. The structure of the oxo complexes was confirmed by single crystal X-ray analysis of $[ReO(SC_6H_4\text{-}2\text{-}F)_3(PPh_3)]$ to be tbp with the oxo ligand occupying one equatorial site.

5. Supplementary material

A complete listing of the crystallographic methods and details has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147162. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

D.M.M. and R.R would like to thank the DGEP–UNAM for Ph.D. scholarships. We are also indebted to Hermann Starck, GmbH for the generous gift of rhenium metal.

References

[1] J.R. Dilworth, J. Hu, Adv. Inorg. Chem. 40 (1994) 411.

[2] I. Bertini, H.B. Gray, S.J. Lippard, J.S. Valentine, Bioinorganic Chemistry, University Science Books, USA, 1994 Ch. 7.

[3] (a) H. Torrens, Coord. Chem. Rev. 196 (2000) 331 and references cited therein. (b) H. Torrens, Trends Organomet. Chem. 1 (1994) 523 and references cited therein.

[4] (a) A.F. Browning, A.D. Bacon, C. White, J. Mol. Catal. 83 (1995) 1. (b) R. Vilar, R. Salcedo, R. Gaviño, T. Ogawa, Eur. Polym. J. 30 (1994) 1237. (c) R. Vilar, R. Salcedo, R. Gaviño, T. Ogawa, Eur. Polym. J. 31 (1995) 1135. (d) F. Monteil, R. Queau, P. Kalck, J. Organomet. Chem. 480 (1994) 177. (e) P. Kalck, P. Escaffre, F. Serein-Spirau, A. Thorez, B. Besson, Y. Colleuille, R. Perron, New. J. Chem. 12 (1988) 687.

[5] F.F. Lahoz, E. Martin, J. Tiburcio, H. Torrens, P. Terreros, Transition Met. Chem. 19 (1994) 381.

[6] D. Cruz-Garritz, J.A. Chamizo, M. Cruz, H. Torrens, Rev. Soc. Quim. Mex. 33 (1989) 18.

[7] J.R. Dilworth, J. Hu, S. Liu, J.A.K. Howard, D.C. Povey, Inorg. Chim. Acta. 223 (1994) 63.

[8] P.J. Blower, J.R. Dilworth, J. Chem. Soc., Dalton Trans. (1985) 2305.

[9] A. Bertrán, H. Torrens, Rev. Soc. Quim. Mex. 37 (1993) 185.

[10] N.P. Johnson, C.J.L. Lock, G. Wilkinson, J. Chem. Soc. (1964) 1054.

[11] J. Chatt, C.D. Falk, G.J. Leigh, R.J. Paske, J. Chem. Soc. A (1969) 2288.

[12] CAD4 Operations Manual, Enraf–Nonius, Delft, 1977.

[13] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[14] G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

[15] L. Zsoluai, ZORTEP—an Ellipsoid Representation Program, University of Heidelberg, 1994.
[16] J.R. Dilworth, J. Hu, J.R. Miller, D.L. Hughes, J.A. Zubieta, Q. Chen, J. Chem. Soc., Dalton Trans. (1995) 3153.
[17] (a) P.J. Blower, J.R. Dilworth, J.P. Hutchinson, T. Nicholson, J.A. Zubieta, Inorg. Chim. Acta 90 (1984) L27. (b) J.R. Dilworth, B.D. Neaves, J.P. Hutchinson, J.A. Zubieta, Inorg. Chim. Acta 65 (1982) L223.
[18] M.E. Peach, Can. J. Chem. 46 (1968) 2699.