The ligand exchange reaction between Re(V)NCl$_2$(PPh$_3$)$_2$ and 2-aminothiophenol: formation of a neutral Re(V) phosphorane thioiminato complex

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Abstract

Reaction of bis(triphenylphosphine)bis(chloro)-nitrido–rhenium(V) with two equivalents of 2-aminothiophenol results in the formation of a neutral, diamagnetic phosphorane thioiminato complex, Re(V)(NPPh$_3$)(2-aminothiophenolato)$_2$, for which the X-ray crystal structure is reported. The compound crystallizes in the monoclinic, $P2_1/c$ space group with $a=12.938(4)$, $b=21.091(7)$, $c=11.578(4)$ Å and $\beta=102.71(3)$°. The nucleophilic attack by the free triphenylphosphine ligand onto the nitrido group is rather unusual. Therefore the neutral oxo complex, Re(V)O(2-aminothiophenolato)$_2$, where one amino group is deprotonated, was synthesized and investigated for its reactivity towards nucleophilic attack by triphenylphosphine. This complex was found to have little such reactivity.

Introduction

The reactivity of metal–oxo complexes towards alkyl phosphines is well known. In the case of Re(V)–oxo and Tc(V)–oxo complexes, several examples of oxygen atom abstraction and two-electron reduction to Re(III) and Tc(III) have been reported [1–4]. The nitrido (N^{3-}) ligand on Ru, Os and Re also exhibits limited activity in the presence of tertiary alkyl phosphines [5–8]. An example of an 'Re(VII)nitrene' compound undergoing nucleophilic attack by triphenylphosphine to form an Re(V)(NPPh$_3$) compound has been reported in the literature [8]. In this reaction, upon coordination by four thiophenolate ligands and exposure to air the Re(V)nitrido compound is oxidized to the electrophilic nitrene, and subsequently, attacked by the nucleophilic tertiary phosphine. We report here the formation of an Re(V)phosphineiminato complex by the reaction between an Re(V)nitrido compound and triphenylphosphine, upon coordination by two bidentate aminothiophenolato ligands.

Because of the reactivity of the nitrido group of the bis-aminothiophenolate-nitrido rhenate(V) complex, we felt that investigation of the reactivity of the oxo group for O-atom transfer for a bis-aminothiophenolato-oxorhenate(V) complex was necessary. Therefore abstraction of oxygen by triphenylphosphine was investigated.

Experimental

Materials

ReNCl$_2$(PPh$_3$)$_2$ and ReOBr$_4^-$nBu$_4$N$^+$ were synthesized according to literature preparations [9, 10]. 2-Aminothiophenol (Hatp) was obtained commercially. Note that neutral aminothiophenol is represented by Hatp, and dissociation of a proton from the mercapto group produces the anion atp$^-$. In the presence of a coordinated metal center a second proton may be dissociated from the ligand, producing a dianion, represented by H$_{-1}$atp^{2-}.

Synthesis of Re(V)(NPPh$_3$)(atp)$_2$

To 0.20 g of ReNCl$_2$(PPh$_3$)$_2$ (0.25 mmol) suspended in benzene under argon, was added a solution of 0.12 ml of 2-aminothiophenol (1.12 mmol) and 0.16 ml of triethylamine (1.12 mmol) in methanol. The mixture was stirred at room temperature for 2 h during which time the suspension disappeared giving a dark orange colored solution. The mixture was refrigerated for 12 h, resulting in the deposit of an orange product which was recrystallized from a chloroform/methanol mixture. The yield was 68% based on rhenium. The compound decomposes at 210–213 °C. ^{1}H NMR at 200 MHz in ^{2}H-chloroform: δ (ppm) 6.7–7.1 (m, 6H) –C$_6$H$_3$; 7.0–7.2 (m, 15H) –C$_6$H$_5$; 7.6–7.8 (m, 2H) –C$_6$H$_3$. IR (KBr pellet): ν(N–P) 1134 cm^{-1}. ^{31}P NMR at 400 MHz in ^{2}H-chloroform shows two singlets at 31.57 and 35.90

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ppm. The FAB$^+$ mass spectrum shows the parent ion $[M-e^-]^+$ at $m/e=711$. Anal. *Calc.* for $C_{30}H_{27}N_3S_2PRe$: C, 50.69; H, 3.83; N, 5.91; P, 4.36. Found: C, 50.26; H, 3.56; N, 5.88; P, 4.20%.

Synthesis of Re(V)O(H$_{-1}$atp)(atp)

To 0.10 g of $ReOBr_4^-nBu_4N^+$ (0.13 mmol) in acetonitrile was added 0.03 ml of 2-aminothiophenol (0.30 mmol) in acetonitrile. The mixture was stirred for 2 h at room temperature. A bright green product which precipitated out was filtered and washed with acetonitrile and water. The yield was 72% based on rhenium. The FAB$^+$ mass spectrum showed the parent ion $[M-e^-]^+$ at $m/e=449$. *Anal.* Calc. for $C_{12}H_{11}N_2S_2$-$ORe\cdot 2H_2O$: C, 50.69; H, 3.83; N, 5.91; P, 4.36. Found: C, 50.26; H, 3.56; N, 5.88; P, 4.20%. IR (KBr pellet): $\nu(Re{=}O)$ 971 cm^{-1}.

The fully deprotonated complex $Re(V)O(H_{-1}atp)_2^-$ was isolated as the nBu_4N^+ salt by addition of nBu_4NBr to the acetonitrile solution described above, immediately after addition of ligand. Precipitation of an olive green product was observed. IR (KBr pellet): $\nu(Re{=}O)$ 936 cm^{-1}. The FAB$^+$ mass spectrum showed the parent ion $[M-2e^-]^+$ as a weak peak at $m/e=449$, and the cation $[nBu_4N^+]$ as a strong peak at $m/e=242$. Negative ion mode shows the parent ion $[M^-]$ at $m/e=449$.

Deprotonation of the phosphineiminato group on $Re(V)(NPPh_3)(atp)_2$ by adding excess $Ph_4AsCl\cdot HCl\cdot H_2O$ to an ethanol solution of the complex open to air results in the formation of an olive green precipitate with spectroscopic properties identical to the anion $[Re(V)O(H_{-1}atp)_2]^-$ described above.

The progress of the O-atom transfer from the metal to triphenylphosphine was followed by detection of the amount of $OPPh_3$ formed by gas chromatographic analysis of the reaction solution. Addition of a ten-fold molar excess of triphenylphosphine to an acetonitrile solution of $Re(V)O(atp)(H_{-1}atp)$ under argon at room temperature results in O-atom abstraction, to form free $OPPh_3$ from 30% of the Re(V) complex. To determine if $Re(V)O(atp)(H_{-1}atp)$ exhibits any catalytic activity, pyridine-*N*-oxide was added to the reaction mixture under argon and the mixture was stirred for 3 days at room temperature. A 70% yield of $OPPh_3$ was observed, based on moles of Re present.

X-ray crystallography

A single-crystal X-ray structural determination was done for $Re(V)(NPPh_3)(atp)_2\cdot CH_2Cl_2$. Full-matrix least-squares was the refinement method used for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. The solution and refinement of the structures were performed on a Nicolet SHELXTL PLUS (Micro Vax II) using direct methods. The structural analyses were performed at the Crystal & Molecular Structure Laboratory, Center for Chemical Characterization and Analysis at Texas A&M University. Data collection, solution and refinement parameters are given in Table 1.

TABLE 1. Summary of crystallographic parameters

Empirical formula	$C_{31}H_{29}N_3PS_2Cl_2Re$
Formula weight	793.7 AMU
a (Å)	12.938(4)
b (Å)	21.091(7)
c (Å)	11.578(4)
β (°)	1102.71(3)
Volume (Å^3)	3082(2)
Temperature (K)	296
Space group	monoclinic, $P2_1/c$ (No. 14)
Formula units/cell	4
Density (calc.) (g/cm^3)	1.711
Radiation	Mo Kα ($\lambda=0.71073$ Å)
Crystal size (mm)	$0.04\times 0.24\times 0.36$
Absorption coefficient (mm^{-1})	4.378
Absorption correction	semi-empirical
Transmission min./max.	0.6060/0.9694
Unique reflections	5429 ($R_{int}=4.91\%$)
Observed reflections	4009 ($F>4.0\sigma(F)$)
Extinction correction	$\chi=0.00004(2)$, where $F^*=F_c[1+0.002\chi F_c^2/\sin(2\theta)]^{-0.25}$
Weighting scheme	$w^{-1}=\sigma^2(F)+0.0001F$
Final residual (obs. data)	$R=4.24\%$, $R_w=3.82\%$
Goodness-of-fit	1.58
Largest and mean Δ/σ	0.001, 0.000
Largest difference peak	1.50
Largest difference hole (ē/Å^3)	−0.94

Results and discussion

$Re(V)NCl_2(PPh_3)_2$ reacts at room temperature under anaerobic conditions with a slight excess of aminothiophenolate anion to give the orange, air-stable $Re(V)(NPPh_3)(atp)_2$. This assignment is verified by the single crystal X-ray structure of the compound.

The compound crystallizes out in the monoclinic, $P2_1/c$ space group with one molecule of CH_2Cl_2 associated with each molecule of Re. The complex is essentially square pyramidal with $NPPh_3^-$ occupying the apical position and the N and S atoms of the aminothiophenolate ligands forming the basal plane of the pyramid. The Re atom lies slightly above the basal plane towards the $(NPPh_3)^-$. This behavior is common for Re(V) compounds with multiply bonded nitrido and oxo groups. A thermal ellipsoid plot of the complex is given in Fig. 1 and the bond lengths and angles are given in Table 2. See also 'Supplementary material'.

The P–N bond length of 1.59 Å falls within the range 1.51–1.66 Å for a P–N double bond [11]. The observed ReNP bond angle of 160°, a significant deviation from linearity, indicates less than triple bond character for the Re–N bond. Another possible reason for the slightly bent ReNP bond is the proximity of the large CH_2Cl_2 solvent molecule.

Because of the limited reactivity exhibited by most metal nitrido compounds, the attack by triphenylphosphine is surprising. The high yield, however, indicates that the reaction is very favorable. The driving force for the attack by PR_3 on an oxo ligand has been attributed to the strength of the resulting phosphine–oxide bond. The driving force to form a multiple P–N bond could also be a driving force in this reaction. Equation (1) shows the probable sequence of events of this reaction. The covalent nature of the bonds formed by the thiolate ligand to the metal allows the nitrido group to be susceptible to electrophilic attack by triphenylphosphine. The phosphorus atom has the ability to expand its valence to accommodate another lone pair.

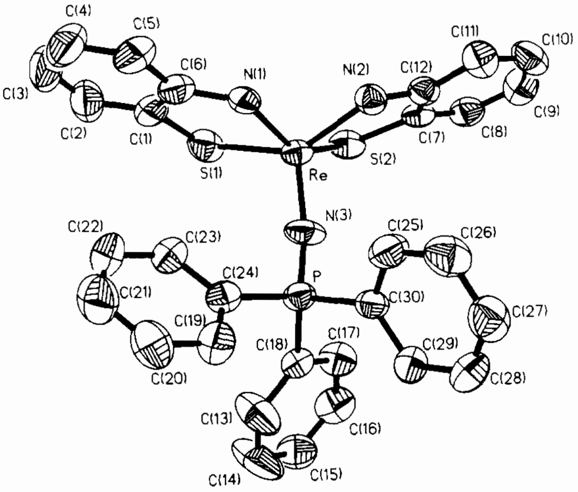
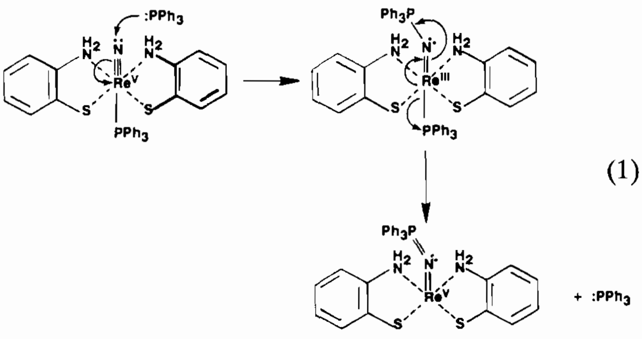


Fig. 1. Thermal ellipsoid (50%) diagram of $Re(NPPh_3)(atp)_2 \cdot CH_2Cl_2$.

TABLE 2. Selected bond lengths (Å) and angles (°) for $C_{31}H_{29}N_3PS_2Cl_2Re$

Re–S(1)	2.311(3)	Re–S(2)	2.317(2)
Re–N(1)	1.953(6)	Re–N(2)	1.966(7)
Re–N(3)	1.799(6)	S(1)–C(1)	1.752(8)
S(2)–C(7)	1.760(9)	P–N(3)	1.595(6)
P–C(18)	1.802(8)	P–C(24)	1.793(7)
P–C(30)	1.805(8)	N(1)–C(6)	1.395(11)
N(2)–C(12)	1.398(10)	C(1)–C(2)	1.395(14)
C(1)–C(6)	1.402(14)	C(2)–C(3)	1.368(18)
C(3)–C(4)	1.373(22)	C(4)–C(5)	1.386(16)
C(5)–C(6)	1.383(12)	C(7)–C(8)	1.392(11)
C(7)–C(12)	1.401(10)	C(8)–C(9)	1.364(15)
C(9)–C(10)	1.387(14)	C(10)–C(11)	1.390(12)
C(11)–C(12)	1.373(13)		
S(1)–Re–S(2)	87.0(1)	S(1)–Re–N(1)	81.1(2)
S(2)–Re–N(1)	141.5(2)	S(1)–Re–N(2)	140.7(2)
S(2)–Re–N(2)	81.0(2)	N(1)–Re–N(2)	85.3(3)
S(1)–Re–N(3)	109.1(2)	S(2)–Re–N(3)	109.5(2)
N(1)–Re–N(3)	109.0(3)	N(2)–Re–N(3)	110.2(3)
Re–S(1)–C(1)	101.1(3)	Re–S(2)–C(7)	101.1(2)
N(3)–P–C(18)	108.4(3)	N(3)–P–C(24)	112.3(3)
C(18)–P–C(24)	110.0(4)	N(3)–P–C(30)	110.6(4)
C(18)–P–C(30)	109.7(3)	C(24)–P–C(30)	105.7(3)
Re–N(1)–C(6)	125.2(6)	Re–N(2)–C(12)	123.9(5)
Re–N(3)–P	160.3(4)	S(1)–C(1)–C(2)	124.5(8)
S(1)–C(1)–C(6)	115.6(7)	C(2)–C(1)–C(6)	119.8(8)
C(1)–C(2)–C(3)	118.8(12)	C(2)–C(3)–(4)	121.4(11)
C(3)–C(4)–C(5)	120.9(11)	C(4)–C(5)–C(6)	118.6(10)
N(1)–C(6)–C(1)	115.9(7)	N(1)–C(6)–C(5)	123.7(9)
C(1)–C(6)–C(5)	120.4(9)	S(2)–C(7)–C(8)	125.4(6)
S(2)–C(7)–C(12)	114.2(6)	C(8)–C(7)–C(12)	120.3(8)
C(7)–C(8)–C(9)	119.6(8)	C(8)–C(9)–C(10)	120.7(8)
C(9)–C(10)–C(11)	119.7(10)	C(10)–C(11)–C(12)	120.5(8)
N(2)–C(12)–C(7)	117.5(8)	N(2)–C(12)–C(11)	123.5(7)
C(7)–C(12)–C(11)	119.0(7)		



(1)

The Re(V)–oxo–bis(aminothiophenolato) complexes were also synthesized to investigate their reactivity towards triphenylphosphine. The neutral Re(V)-$O(H_{-1}atp)(atp)$ was synthesized by a simple ligand exchange reaction with $Re(V)OBr_4^-$. Deprotonation of one of the amino groups is observed. Deprotonation of an amino group of aminothiophenol upon coordination by a metal ion has been well documented in the literature, and includes a Tc(V)O complex [12–14].

The O-atom transfer from the metal to triphenylphosphine occurs in about a 70% yield after 3 days. Therefore, we conclude that, under the conditions employed, the reaction must be stoichiometric, and catalytic O-atom transfer does not occur.

Supplementary material

Tables listing hydrogen atom and structural parameters, structure factors, interatomic distances and torsion angles are available from the authors.

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References

1 J. Lu and M.J. Clarke, *Inorg. Chem., 27* (1988) 4761.
2 N. deVries, A.G. Jones and A. Davison, *Inorg. Chem., 28* (1989) 3729.
3 R.R. Conry and J.M. Mayer, *Inorg. Chem., 29* (1990) 4862.
4 J. Lu, A. Yamano and M.J. Clarke, *Inorg. Chem., 29* (1990) 3483.
5 W.P. Griffith and D. Pawson, *J. Chem. Soc., Chem. Commun.*, (1973) 418.
6 F.L. Phillips and A.C. Skapski, *J. Chem. Soc., Chem. Commun.*, (1974) 49.
7 K. Dehnicke and J. Strahle, *Polyhedron, 8* (1989) 707.
8 J.R. Dilworth and B.D. Neaves, *Inorg. Chim. Acta, 65* (1982) L223.
9 J. Chatt, J.D. Garforth, N.P. Johnson and G.A. Rowe, *J. Chem. Soc.*, (1964) 1012.
10 F.A. Cotton and S.J. Lippard, *Inorg. Chem., 5* (1966) 9.
11 L.B. Handy, J.K. Ruff and L.F. Dahl, *J. Am. Chem. Soc., 92* (1970) 7327.
12 G. Bandoli and T.I.A. Gerber, *Inorg. Chim. Acta, 126* (1987) 205.
13 A.L. Balch and R.H. Holm, *J. Am. Chem. Soc., 88* (1966) 5201.
14 E.I. Stiefel, J.H. Waters, E. Billig and H.B. Gray, *J. Am. Chem. Soc., 87* (1965) 3016.