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# The first family of trigonal prismatic M(bidentate)<sub>2</sub>(monodentate)<sub>2</sub> complexes: synthesis and characterization of halobis(2amidothiophenolato)triphenylphosphinerhenium(V)

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#### Abstract

The 1:2 reaction of  $[\text{Re}^{V}\text{OCl}_{3}(\text{PPh}_{3})_{2}]$  with 2-aminothiophenol (H<sub>2</sub>atp) in toluene has afforded red-brown  $[\text{Re}^{V}(\text{atp})_{2}(\text{Cl})(\text{PPh}_{3})]$ . The corresponding bromo and iodo complexes have been similarly obtained from  $[\text{Re}^{V}\text{O}(\text{OEt})\text{Br}_{2}(\text{PPh}_{3})_{2}]$  and  $[\text{Re}^{V}\text{O}(\text{OEt})\text{I}_{2}(\text{PPh}_{3})_{2}]$ , respectively. The X-ray structure of the solvate  $[\text{Re}(\text{atp})_{2}(\text{Cl})(\text{PPh}_{3})] \cdot 2\text{CH}_{2}\text{Cl}_{2}$  has revealed trigonal prismatic geometry for the  $\text{ReS}_{2}N_{2}\text{ClP}$  coordination sphere in which the two triangular faces are defined by the S, S,P and N, N, Cl triads. The twist angle between them is 8.0°. The  $[\text{Re}(\text{atp})_{2}(\text{X})(\text{PPh}_{3})](\text{X} = \text{Cl}, \text{ Br}, \text{ I})$  complexes are diamagnetic  $(\text{Re}^{V}, \text{ spin-paired } d^{2})$  and in acetonitrile solution these display a quasireversible  $\text{Re}^{VI}$ – $\text{Re}^{V}$  response near 0.7 V. Reaction with H<sub>2</sub>atp in air converts  $[\text{Re}^{V}(\text{atp})_{2}(\text{X})(\text{PPh}_{3})]$  to the tris chelate  $[\text{Re}^{VI}(\text{atp})_{3}]$ . © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Rhenium complexes; Trigonal prismatic geometry; 2-Amidothiophenolato complexes

## 1. Introduction

The trigonal prism is rarely favoured over the octahedron as the geometry of hexacoordination in molecular transition metal chemistry. Bonding theories indicate that metal ions with few d-electrons may assume the rare geometry in combination with strongly  $\sigma$ -donating nonbulky ligands [1–3]. Model examples are WMe<sub>6</sub> [4,5] and ZrMe<sub>6</sub><sup>2-</sup> [6–8]. In practice, however, trigonal prismatic molecules have remained primarily confined to the tris chelate family, M(bidentate)<sub>3</sub> where indeed such species were first discovered [9–11]. The bidentate ligands are formally dianionic and span the donor types SS [11–13], SeSe [11], PP [14], NN [15] and SN [15–18].

Tris chelates undoubtedly have the advantages of facile synthesis and convenient geometrical definition in terms of a threefold axis. However, the paucity of other types having trigonal prismatic geometry is an untenable position specially in terms of chemical synthesis. This has prompted us to search for such types and the logical first target is the bischelate system  $M(bidentate)_2(mo-nodentate)_2$ . Herein we disclose the synthesis and characterization of the first family representing the system.

### 2. Experimental

#### 2.1. General considerations

The starting materials  $[ReOCl_3(PPh_3)_2]$ ,  $[ReO(OEt)Br_2(PPh_3)_2]$  and  $[ReO(OEt)I_2(PPh_3)_2]$  were prepared by reported methods [19,20]. 2-Aminothiophenol was purchased from Fluka (Switzerland). The purification and drying of dichloromethane and acetonitrile for synthesis as well as electrochemical and spectral work were done as before [21,22].

Toluene was distilled over sodium before use. All other chemicals and solvents were of reagent grade and were used as received.

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UV–Vis spectra (CH<sub>2</sub>Cl<sub>2</sub> solution), IR spectra (KBr disk), and <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) were recorded on a Shimadzu UVPC 1601 spectrophotometer, a Perkin–Elmer 783 spectrometer, and a Bruker FT 300 MHz spectrometer, respectively. The numbering scheme used for <sup>1</sup>H NMR assignment is the same as in crystallography. Spin-spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Cyclic voltammetry (in MeCN, 0.1M TEAP) was done at a platinum working electrode under nitrogen atmosphere on a PAR model 370-4 electrochemistry system [23]. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 Series II elemental analyzer.

# 2.2. Synthesis of chlorbis(2amidothiophenolato)triphenylphosphinerhenium(V), [Re(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)] (2a)

To a suspension of ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (100 mg, 0.120 mmol) in 10 ml of toluene was added 30 mg (0.240 mmol) of 2-aminothiophenol, (H<sub>2</sub>atp). The resulting mixture was heated to reflux for 15 min affording a reddish brown solution. The solvent was then removed under reduced pressure, and the solid thus obtained was dissolved in 5 ml of dichloromethane, and the solution was subjected to chromatography on a silica gel column  $(20 \times 1 \text{ cm}; 60-120 \text{ mesh}, \text{BDH})$ . A deep reddish brown band was eluted out with a benzene-acetonitrile (25:1) mixture. Removal of solvent under reduced pressure afforded the pure complex which was dried in vacuo over fused calcium-chloride Yield: (57 mg, 65%). Anal Calc. for C<sub>30</sub>H<sub>25</sub>ClN<sub>2</sub>S<sub>2</sub>PRe: C, 49.34; H, 3.45; N, 3.84. Found: C, 49.28; H, 3.49; N, 3.87%. UV–Vis (λ<sub>max</sub>, nm  $(\varepsilon, M^{-1}cm^{-1})$ : 447(11450); 326(5730). IR(cm<sup>-1</sup>, KBr pellet): 3250(NH), 320(Re–Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : H5, H11 7.80 (d, J 8.1 Hz); H2, H8 7.56 (d, J 8.4 Hz); H4, H10 7.08 (t, J 7.2 Hz); H3, H9 6.92 (t, J 7.3 Hz). N-H, 12.46(s); aromatic multiplets, 7.28-7.48.

# 2.3. Synthesis of bromobis(2amidothiophenolato)triphenylphosphinerhenium(V), [Re(atp)<sub>2</sub>(Br)(PPh<sub>3</sub>)] (2b)

To suspension of [ReO(OEt)Br<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.102 mmol) in 10 ml of toluene was added 25.6 mg (0.204 mmol) of 2-aminothiophenol, H<sub>2</sub>atp. The same procedure as in the previous preparation was then followed affording the reddish brown complex. Yield: (53.9 mg, 68%). *Anal.* Calc. for C<sub>30</sub>H<sub>25</sub>BrN<sub>2</sub>S<sub>2</sub>PRe: C, 46.51; H, 3.25; N, 3.62. Found: C, 46.46; H, 3.29: N, 3.65%. UV–Vis ( $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 453(6740); 335(4284). IR (cm<sup>-1</sup>, KBr pellet): 3252(NH). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : H5, H11 7.89 (d, *J* 8.0 Hz); H2, H8 7.65 (d, *J* 8.3 Hz); H4, H10 7.15 (t, *J* 7.5 Hz). H3, H9 7.03 (t, *J* 7.4 Hz); N–H 12.77(s); aromatic multiplets, 7.28–7.35. 2.4. Synthesis of iodobis(2amidothiophenolato)triphenylphosphinerhenium(V), [Re(atp)<sub>2</sub>(I)(PPh<sub>3</sub>)] (**2c**)

This was synthesized in the same manner as (**2b**) using [ReO(OEt)I<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.098 mmol) and H<sub>2</sub>atp (24.4 mg, 0.196 mmol) Yield: (52 mg, 65%). *Anal* Calc. for C<sub>30</sub>H<sub>25</sub>IN<sub>2</sub>S<sub>2</sub>PRe: C, 43.84; H, 3.06; N, 3.41. Found: C, 43.78; H, 3.11; N, 3.45%. UV–Vis ( $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 463(8090); 347(8760). IR (cm<sup>-1</sup>, KBr pellet): 3250 (NH). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : H5, H11 7.93 (d, *J* 7.7 Hz); H2, H8 7.67 (d, *J* 8.4 Hz). H4, H10 7.12(m); H3, H9 7.12(m); N–H 13.08(s); aromatic multiplets, 7.33–7.52.

# 2.5. Conversion of $[Re(atp)_2(Cl)(PPh_3)]$ to $[Re(atp)_3]$

To a solution of  $[\text{Re}(\text{atp})_2(\text{Cl})(\text{PPh}_3)]$  (100 mg, 0.137 mmol) in 10 ml of toluene was added 17.12 mg (0.137 mmol) of H<sub>2</sub>atp. The resulting mixture was heated to reflux for 60 min affording a deep green solution. The solvent was then removed under reduced pressure and the solid thus obtained was dissolved in 10 ml of acetone and kept for slow evaporation for a few days to get the pure complex which was dried in vacuo over fused calcium chloride, Yield: (62.3 mg, 83%). The [Re(atp)<sub>2</sub>(Br)(PPh<sub>3</sub>)] and [Re(atp)<sub>2</sub>(I)(PPh<sub>3</sub>)] complexes could be similarly converted to [Re(atp)<sub>3</sub>].

#### 2.6. X-ray crystallography

Single crystal of  $[\text{Re}(\text{atp})_2(\text{Cl})(\text{PPh}_3)].2\text{CH}_2\text{Cl}_2$  were grown by slow diffusion of hexane into dichloromethane solution the crystals rapidly lost the solvent of crystallization and crystallinity in air. A crystal was sealed over the mother liquor for crystallography. Cell parameters were determined by a least-squares fit of 30 machinecentered reflections  $(14^\circ \le 2\theta \le 28^\circ)$ . Data were collected by the  $\omega$  scan technique in the range  $3^\circ \le 2\theta \le$  $50^\circ$  for  $[\text{Re}(\text{atp})_2(\text{Cl})(\text{PPh}_3)]$  on a Siemens R3 m/V fourcircle diffractometer with graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation at 25 °C. Two check reflections after each 198 reflections showed no significant intensity reduction. All data were corrected for Lp effects and absorption [24].

The metal atom was located from Patterson maps, and the rest of the nonhydrogen atoms emerged from successive Fourier synthesis. The structure were refined by full-matrix least-squares procedures on  $F^2$ . All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions. Calculations were performed using the SHELXTL V5.03 [25] program package. The two dichloromethane molecules in the lattice are disordered. Significant crystal data are listed in Table 1.

Table 1 Crystallographic data for [Re<sup>V</sup>(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)]·2 CH<sub>2</sub>Cl<sub>2</sub> (2a)

Empirical formula	$C_{32}H_{28}Cl_5N_2PReS_2$
Formula weight	899.10
Crystal system	triclinic
Space group	ΡĪ
a (Å)	9.693 (3)
b (Å)	13.529 (5)
c (Å)	14.944 (4)
α (°)	115.61 (2)
β (°)	97.78 (2)
γ (°)	92.27 (3)
V (Å <sup>3</sup> )	1740.2 (10)
Z	2
$D_{\text{calc.}}$ (Mg m <sup>-3</sup> )	1.716
$\mu  ({\rm mm}^{-1})$	4.067
$\theta$ Range (°)	1.70-25.00
$R^{a}, wR_2^{b}[I > 2\sigma(I)]$	0.0744, 0.1796
Goodness-of-fit on $F^2$	1.046

<sup>a</sup>  $R = ||F_{\rm o}| - |F_{\rm c}||/\Sigma|F_{\rm o}|.$ 

<sup>b</sup> 
$$wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}.$$

The twist angle ( $\phi$ ) is defined and calculated according to a published procedure [26]. In the case of [Re(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)], let cen a and cen b be the centroids of the faces N1, N2, Cl1 and S1, S2, P1, respectively. The dihedral angles between planes of cen a, cen b, N1 and cen a, cen b S1; cen a, cen b, N2 and cen a, cen b, S2 and cen a, cenb, Cl1 and cen a, cen b P1 are respectively  $5.5^{\circ}$ ,  $8.8^{\circ}$  and  $9.7^{\circ}$ . The average value,  $8.0^{\circ}$ , is taken as  $\phi$ . The angular parameters for [Re(atp)<sub>3</sub>] were either taken directly from the published work or were computed using the available atomic coordinates [15]. Here the twist angle is  $7.9^{\circ}$  is the average of the three dihedral angles  $7.4^{\circ}$ ,  $7.8^{\circ}$  and  $8.5^{\circ}$  between planes defined in the same manner as in the case of [Re(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)].

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The bidentate ligand used in the present work is 2aminothiophenol ( $H_2atp$ ) which is prone to chelate metal ions in diionised form as in (1). The basis of this choice is the



proven ability of this ligand to stabilize the trigonal prismatic geometry upon tris chelation as in  $[Re^{VI}(atp)_3]$  [15,16],  $[Tc^{VI}(atp)_3]$  [27] and  $[Mo^{VI}(atp)_3]$  [28].

The reaction of  $[Re^{V}OCl_{3}(PPh_{3})_{2}]$  with H<sub>2</sub>atp in boiling toluene afforded a reddish brown solution from which  $[Re^{V}(atp)_{2}(Cl)(PPh_{3})]$  of coordination type (2a) could indeed be isolated in satisfactory yield. For the success of the synthesis it is crucial to control both the reaction time (15 min) and metal: ligand (1:2) mole ratio. Use of  $[Re^{V}O(OEt)Br_2(PPh_3)_2]$  and  $[Re^{V}O(OE-t)I_2(PPh_3)_2]$  in place of  $[Re^{V}OCl_3(PPh_3)_2]$  in the above synthesis afforded the bromo (2b) and iodo (2c) complexes, respectively.



Our interest in oxorhenium chemistry [29-31] prompted us to examine the above Re<sup>V</sup>O reagents incorporating X(Cl, Br, I) and PPh<sub>3</sub> coligands as starting materials for the reaction with H<sub>2</sub>atp. It was hoped that ionised H<sub>2</sub>atp would displace the oxo atom forming chelate rings of type (1) but with retention of some X/PPh<sub>3</sub> coordination. This happened in practice.

Selected characterization data for (2a-2c) are given in the Section 2. The complexes are uniformly diamagnetic corresponding to the spin paired d<sup>2</sup> configuration (idealized  $a_1^{(2)}$  [1]. In solution the complexes display two characteristic allowed bands in the UV–Vis region. Their energy decreases slightly as in the order (2a) (447, 326 nm) > (2b)(453, 335 nm) > (2c) (463 nm, 347 nm). In IR the N–H stretch is seen as a sharp feature near 3250 cm<sup>-1</sup>.

The two coordinated  $atp^{2-}$  ligands are equivalent in solution giving rise to two <sup>1</sup>H NMR doublets and two triplets in the aromatic region, 6.5–8.0 ppm (*J*, 7.0–8.5 Hz). The N–H proton resonance occurs as a characteristic singlet at 12.46°, 12.77° and 13.08 ppm for (**2a**), (**2b**) and (**2c**), respectively. The signal 'disappears' upon addition of D<sub>2</sub>O to the solution.

#### 3.2. Crystal and molecular structure

Only complex (2a) afforded single crystals in the form of loosely held solvate  $(2a) \cdot 2CH_2Cl_2$  which was stable only in presence of the mother liquor. A molecular view of the complex is shown in Fig. 1 and selected bond parameters are listed in Table 2. The  $CH_2Cl_2$  molecules are highly disordered and occupy cavities in the lattice.

The  $\text{ReS}_2\text{N}_2\text{ClP}$  coordination sphere has distorted trigonal prismatic geometry as in (2a). The synthetic procedure used always afforded the same complex and no evidence of the existence of the possible geometrical isomers could be found. The areas of the triangular faces defined by S1, S2, P1 and N1, N2, Cl1 are 4.38 and 3.97 Å<sup>2</sup>, respectively. The prism is thus tapered.



Fig. 1. Molecular view and atom-labeling scheme for  $[Re(atp)_2(Cl)(PPh_3)]$ . All nonhydrogen atoms are represented by 30% thermal probability ellipsoids.

Certain angular parameters diagnostic of the geometry are: twist angle ( $\phi$ ), dihedral angle ( $\omega_1$ ) between one coordination plane and another, dihedral angle ( $\omega_2$ ) between a coordination plane and a triangular face and angle ( $\theta$ ) at the metal site between two donors in *trans* positions. In the present complex the  $\phi$  value is 8.0°. The other angles (Table 2) span the ranges:  $\omega_1$ , 113.7°– 124.7°;  $\omega_2$ , 80.2°–98.7° and  $\theta$ , 123.3°–142.7°. It is instructive to compare these parameters with those of the structurally characterized tris chelate [Re(atp)<sub>3</sub>] [15] as well as with those of idealised  $D_{3h}$  and  $O_h$  geometries (Table 3).

Whereas the span of the angular parameters of  $[Re(atp)_2(Cl)(PPh_3)]$  is generally higher, the averages invariably lie close to those in  $[Re(atp)_3]$ .

Even though the metal oxidation state in  $[Re(atp)_2(Cl)(PPh_3)]$  is lower than that in  $[Re(atp)_3]$ 

Table 3 Angular parameters <sup>a</sup> of [Re(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)]·2CH<sub>2</sub>Cl<sub>2</sub> and [Re(atp)<sub>3</sub>]

Parameters <sup>b</sup>	[Re(atp) <sub>2</sub> (Cl)(PPh <sub>3</sub> )]	[Re(atp) <sub>3</sub> ]	$D_{3h}$	$O_h$
$\phi (°) \\ \omega_1 (°) \\ \omega_2 (°) \\ \theta (°)$	8.0	7.9	0	60
	113.7-124.7(119.3)	119.0–119.8(119.3)	120	90
	80.2-98.7(90.5)	84.4–95.1(91.4)	90	54.7
	123.3-142.7(134.4)	128.2–140.3(134.3)	135.6	180

<sup>a</sup> Average values are given in parenthesis.

<sup>b</sup> For definition see text.

the average Re–N (1.97 Å) and Re–S (2.30 Å) lengths in the former are slightly shorter than those (2.00 and 2.35 Å, respectively) in [Re(atp)<sub>3</sub>] [15]. In absence of the third chelate ring the two atp<sup>2–</sup> ligands are pulled closer to the metal in [Re(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)]. We are unable to compare the Re–Cl(2.438(3)) and Re–P (2.450(4)) lengths with those in other trigonal prismatic systems, since no such system exist. In pseudooctahedral species Re<sup>V</sup>–Cl [29–31] and Re<sup>V</sup>–P [20,32,33] lengths usually lie in the ranges 2.31–2.39 and 2.46–2.52 Å, respectively.

The similarity of the properties of (2b) and (2c) with those of (2a) strongly suggest that the former species also have gross trigonal prismatic geometry, although the extent of distortion could be different in the three species. We thus have here the first examples of the trigonal prismatic complexes of type M(bidentate)<sub>2</sub>(monodentate)<sub>2</sub>. Further unusual feature of (2) include the presence of the bulky PPh<sub>3</sub> as a ligand and the presence of the d<sup>2</sup> metal ion (Re<sup>V</sup>). Structurally characterized trigonal prismatic metal complexes of good standing (using  $\phi < 10^{\circ}$  as a criterion) generally contain only d<sup>0</sup> or d<sup>1</sup> metal ions [9–11,14,15,18,27,28]. We are excluding

Table 2

Selected bond distances (Å) angles (°) and dihedral angles (°) for [Re(atp)<sub>2</sub>(Cl)(PPh<sub>3</sub>)]·2CH<sub>2</sub>Cl<sub>2</sub> (2a)

Bond distances				
Re-N(1)	1.956(11)		Re-N(2)	1.988(12)
Re-S(1)	2.306(4)		Re-S(2)	2.289(4)
Re-Cl(1)	2.438(3)		Re-P(1)	2.450(4)
Bond angles				
N(1)-Re-S(1)	79.0(3)		N(1)-Re-S(2)	142.7(3)
N(2)-Re-S(1)	134.0(4)		N(2)-Re-S(2)	79.1(4)
N(1)-Re-N(2)	86.7(5)		S(1)-Re-S(2)	86.5(2)
N(1)-Re-Cl(1)	82.2(3)		N(1)-Re-P(1)	123.3(3)
N(2)-Re-Cl(1)	81.4(4)		N(2)-Re-P(1)	140.2(4)
S(1)-Re-Cl(1)	137.9(2)		S(1)-Re-P(1)	81.4(13)
S(2)-Re-Cl(1)	128.5(2)		S(2)-Re-P(1)	87.5(14)
Cl(1)-Re-P(1)	78.1(12)			
Dihedral angles				
Re, N(1), S(1)–Re, N(2), S(2) 124.7	Re, N(1), S(1)-Re, P(1), Cl(1)	113.7		
Re, N(2), S(2)–Re, P(1), Cl(1) 119.4				
Re, N(1), S(1)-Cl(1), N(1), N(2) 80.2	Re, N(1), S(1)-P(1), S(1), S(2)	86.5		
Re, N(2), S(2)–Cl(1), N(1), N(2) 93.5	Re, N(2), S(2)-P(1), S(1), S(2)	86.5		
Re, Cl(1), P(1)-Cl(1), N(1), N(2) 98.7	Re, Cl(1), P(1)-P(1), S(1), S(2)	97		

the cases where the geometry is forced by ligand structure (clathro-chelates) [34].

#### 3.3. Metal redox and reaction with $H_2$ atp

In acetonitrile solution the  $[\text{Re}(\text{atp})_2(\text{Cl})(\text{PPh}_3)]$  species display a quasireversible cyclic voltrametric response near 0.7 V versus SCE (Table 4). The response is assigned to the  $\text{Re}^{\text{VI}}-\text{Re}^{\text{V}}$  couple, the reduction potential of which decreases slightly in the order (2a) > (2b) > (2c).

Upon treating the type (2) species with one mole of  $H_2$ atp in boiling toluene in air for 1 h, the PPh<sub>3</sub> and X<sup>-</sup> ligands are replaced by atp<sup>2-</sup> affording the tris chelate [Re(atp)<sub>3</sub>] in excellent yield. In this reaction the metal undergoes spontaneous aerial oxidation (Re<sup>V</sup>  $\rightarrow$  Re<sup>VI</sup>). This happens because of the large decrease in the Re<sup>VI-</sup> Re<sup>V</sup> reduction potential ( $E_{1/2}$  of [Re(atp)<sub>3</sub>], -0.12 V [16]) upon tris chelation. The stabilization of the d<sup>2</sup> configuration (Re<sup>V</sup>) in the present complex is promoted by the PPh<sub>3</sub>, X pair of ligands.

#### 4. Conclusion

The synthesis and characterization of the first family of trigonal prismatic complexes,  $[Re^{V}(atp)_{2}(X)(PPh_{3})]$ , belonging to type M(bidentate)<sub>2</sub> (monodentate)<sub>2</sub> has been achieved by reacting Re<sup>V</sup>O reagents with H<sub>2</sub>atp. The species are further unusual in having a bulky ligand (PPh<sub>3</sub>) and d<sup>2</sup> configuration.

Pentavalent rhenium is redox stabilized in the family by the PPh<sub>3</sub>, X ligand pair. The complexes react with H<sub>2</sub>atp in air affording the tris chelate  $[Re^{VI}(atp)_3]$  where the hexavalent metal is stabilized. Further work on the design and isolation of different molecular trigonal prismatic chelate type are in progress.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 174267 for compound (2a). Copies of this information may be obtained free of

Table 4

Cyclic voltametric data in acetonitrile solution (0.1 M TEAP) <sup>a</sup>

$\frac{E_{1/2}/\mathrm{V}(\Delta E_\mathrm{p}/\mathrm{mV})}{\mathrm{Re^{VI}/Re^{V}}}$	
0.72(80)	
0.70(120)	
0.68(120)	
	$\frac{\frac{E_{1/2}/V(\Delta E_{p}/mV)}{Re^{VI}/Re^{V}}}{0.72(80)}$ 0.70(120) 0.68(120)

<sup>a</sup> Conditions: working electrode, platinum; reference electrode, SCE; scan rate 50 mV s<sup>-1</sup>.  $E_{1/2} = 1/2$  ( $E_{pa} + E_{pc}$ ), where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials, respectively,  $\Delta E_p = E_{pa} - E_{pc}$ .

charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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