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# Note

# Rhenium polyhydrides stabilized by arsine ligands

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#### Abstract

The mixed phosphine-arsine ligand  $Ph_2PCH_2CH_2AsPh_2$  (arphos) has been used to stabilize the rhenium polyhydrides  $Re_2H_8(arphos)_2$ and  $ReH_7(arphos)$ . The heptahydride is the first example of a compound of the type  $ReH_7L_2$  which contains a mixed phosphine-arsine donor set. The spectroscopic and electrochemical properties and stabilities of these complexes are described and compared with data for other complexes of the types  $Re_2H_8L_4$  and  $ReH_7L_2$ .

Keywords: Rhenium complexes; Polyhydride complexes; Arsine complexes

# 1. Introduction

In a recent report in this journal, Loza and Crabtree [1] described the isolation of  $\text{ReH}_7(\text{AsPh}_3)_2$ , its spectroscopic properties, and some preliminary explorations of its reactions. These workers also commented on the apparent paucity of rhenium polyhydride complexes in which arsine ligands are present. In this Note, we describe examples of rhenium polyhydrides which contain the mixed phosphine/arsine ligand  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$  (arphos) and draw attention to the extensive series of dirhenium polyhydride complexes of the type  $\text{Re}_2\text{H}_8\text{L}_4$ , in which L can represent a phosphine, arsine or stibine ligand.

#### 2. Experimental

# 2.1. Starting materials and procedures

A standard procedure was used to prepare ReOCl<sub>3</sub>(arphos) [2]. A mixture of KReO<sub>4</sub> (0.418 g, 1.45 mmol), arphos (1.053 g, 2.38 mmol), and conc. aqueous HCl (10 ml) was refluxed for 24 h in n-propanol (70 ml). The blue precipitate was filtered off, washed with ethanol ( $5 \times 15$  ml) and dried under vacuum; yield 0.902 g (83%). The dirhenium(II) complex Re<sub>2</sub>Cl<sub>4</sub>( $\mu$ -arphos)<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>CO was prepared with the use of a procedure similar to that described for its Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (dppe) analogue [3], except that Re<sub>2</sub>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>(py)<sub>2</sub> was used in place of

Re<sub>2</sub>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> and the ratio of reactants (dirhenium complex:arphos) was decreased from 1:4 (for dppe) to 1:2. The reaction was carried out in refluxing acetone for 24 h; yield 52%. The identity of this starting material, as prepared by this new procedure, was established on the basis of its electrochemical properties [4]. The ligand 1-diphenylphosphino-2-diphenylarsinoethane (arphos) was purchased from Strem Chemical Co. or Chem Service, Inc. Solvents and other reagents were purchased from commercial sources. THF was freshly distilled and all solvents were thoroughly deoxygenated prior to use. All reactions were performed under a dry nitrogen atmosphere with the use of standard vacuum line techniques. A 3 foot 18-gauge cannula was used for transferring some of the reaction mixtures.

# 2.2. Reaction of $Re_2Cl_4(arphos)_2 \cdot (CH_3)_2CO$ with LiAlH<sub>4</sub>. Synthesis of $Re_2H_8(arphos)_2$

A quantity of LiAlH<sub>4</sub> (0.136 g, 3.58 mmol) was added slowly to a suspension of  $\text{Re}_2\text{Cl}_4(\text{arphos})_2 \cdot (\text{CH}_3)_2\text{CO}$ (0.264 g, 0.181 mmol) in 20 ml of THF. This green colored mixture was stirred overnight at room temperature. The suspension was then hydrolyzed with a mixture of 5 ml of deoxygenated H<sub>2</sub>O and 15 ml of THF. At this point the mixture was heated gently for 3 h, during which time the solution gradually turned orange. The reaction mixture was filtered through Celite by using a cannula in the transfer. The resulting filtrate was evaporated and the residue dissolved in about 5 ml of THF. An excess of methanol (~20 ml) was added to precipitate a red-orange powder, which was filtered off using a cannula, washed with methanol, and dried in vacuo; yield

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0.136 g (60%). Anal. Calc. for  $C_{52}H_{56}P_2As_2Re_2$ : C, 49.37; H, 4.46. Found: C, 49.03; H, 4.34%.

# 2.3. Reaction of ReOCl<sub>3</sub>(arphos) with *MaBH*<sub>4</sub>. Synthesis of ReH<sub>7</sub>(arphos)

A suspension of ReOCl<sub>3</sub>(arphos) (0.870 g, 1.16 mmol) in 45 ml of ethanol was placed in an acetone/ice bath. Then an excess of NaBH<sub>4</sub> (0.96 g, 25.4 mmol) was added and the green reaction mixture stirred for about 9 h while the reaction mixture was allowed to warm slowly to room temperature. When the solution had turned a pale orange color, the solvent was evaporated. Approximately 20 ml of hexanes were added to the residue and the resulting slurry stirred for about 20 min, after which it was evaporated. The reaction flask was then flushed with  $N_2(g)$  and the residue extracted with benzene and filtered through Celite. This procedure was repeated until the extract was colorless. The resulting brown filtrate was evaporated and the residue then dissolved in freshly distilled THF (10 ml). This solution was concentrated and placed in the freezer overnight. The resulting pale yellow crystals were filtered off and rinsed with cold, distilled THF and pentane. The white solid was dried in vacuo; yield 0.284 g (40%). Anal. Calc. for C<sub>26</sub>H<sub>31</sub>AsPRe: C, 49.13; H, 4.92. Found: C, 49.25; H, 5.14%.

When the aforementioned reaction between ReOCl<sub>3</sub>-(arphos) (0.220 g, 0.293 mmol) and NaBH<sub>4</sub> (0.217 g, 5.73 mmol) was carried out in *refluxing* ethanol for 1 h, a crop of Re<sub>2</sub>H<sub>8</sub>(arphos)<sub>2</sub> was obtained. The orange powder was filtered off, washed with ethanol ( $2 \times 15$  ml) and methanol ( $2 \times 15$  ml) and dried under vacuum; yield 0.031 g (16%). The identity of this product was established from a comparison of its spectroscopic and electrochemical properties with those of the sample prepared in Section 2.2.

A procedure similar to that described above for the synthesis of RcH<sub>7</sub>(arphos) was used to prepare ReH<sub>7</sub>(dppe) from ReOCl<sub>3</sub>(dppe). The product was recrystallized twice from freshly distilled THF and dried under vacuum; yield 52%. This is a modification of a procedure reported by Chatt and Coffey [5], which uses the reaction of ReOCl<sub>3</sub>(dppe) with LiAlH<sub>4</sub> in THF. The identity and purity of our samples was confirmed by NMR spectroscopy.

### 2.4. Physical measurements

IR spectra, NMR spectra and cyclic voltammograms were determined as described previously [6].

# 3. Results and discussion

The dirhenium polyhydride complex  $\text{Re}_2\text{H}_8(\text{arphos})_2$  can be prepared in good yield by the reaction of the triply bonded dirhenium(II) complex  $\text{Re}_2\text{Cl}_4(\mu\text{-arphos})_2$  with LiAlH<sub>4</sub> in THF, followed by hydrolysis of the reaction mixture and workup. This procedure resembles that used previously to obtain a variety of phosphine containing complexes of the type  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$  ( $\text{PR}_3 = \text{PMe}_3$ ,  $\text{PEt}_3$ ,  $\text{P-n-Pr}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PEt}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $1/2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$  or  $1/2(\text{Ph}_2\text{PCH}_2\text{-}C\text{H}_2\text{PPh}_2)$ ) [7]. This is the first arsine stabilized dirhenium polyhydride to be prepared directly from a dirhenium(II) precursor complex.  $\text{Re}_2\text{H}_8(\text{arphos})_2$  is also formed upon refluxing a mixture of mononuclear  $\text{ReOCl}_3(\text{arphos})$  with NaBH<sub>4</sub> in ethanol, presumably through the intermediacy of the mononuclear heptahydride  $\text{ReH}_7(\text{arphos})$ , which is the product when the reaction is carried out at low temperature (vide infra). The thermal decomposition of certain mononuclear complexes of the type  $\text{ReH}_7(\text{PR}_3)_2$  to afford the dinuclear species  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$  is well documented [5,7,8].

The complex  $\text{Re}_2\text{H}_8(\text{arphos})_2$  exhibits electrochemical behavior which is similar to that reported previously for other dirhenium octahydride complexes, including  $\text{Re}_2\text{H}_8(\text{dppe})_2$ [7]. The cyclic voltammogram (CV) of a solution of  $\text{Re}_2\text{H}_8(\text{arphos})_2$  in 0.1 M TBAH–CH<sub>2</sub>Cl<sub>2</sub> shows a reversible couple at  $E_{1/2}(\text{ox}) = -0.03$  V versus Ag/AgCl. The corresponding process in the CV of  $\text{Re}_2\text{H}_8(\text{dppe})_2$  is at  $E_{1/2}(\text{ox}) = -0.02$  V versus Ag/AgCl [7]. The Nujol mull IR spectrum of  $\text{Re}_2\text{H}_8(\text{arphos})_2$  shows a fairly intense  $\nu$  (Re– H) mode at 1946 cm<sup>-1</sup>, which compares with a value of 1970 cm<sup>-1</sup> reported for  $\text{Re}_2\text{H}_8(\text{dppe})_2$  [7].

The <sup>1</sup>H NMR spectra of solutions of  $Re_2H_8(arphos)_2$  in  $CD_2Cl_2$  and  $C_6D_6$  display a binomial triplet ( $^2J(P-H) = 9.5$ Hz) for the Re-H resonance at  $\delta - 7.20$  and -6.51, respectively. This observation confirms the fluxional nature of this complex, with eight equivalent hydrides being split by two equivalent P nuclei. For the analogous complex  $Re_2H_8(dppe)_2$ , this resonance appears as a binomial pentet at  $\delta = 6.62$  and -6.01, respectively, in these two solvents [7]. The variable temperature <sup>1</sup>H NMR spectrum of Re<sub>2</sub>H<sub>8</sub>(arphos)<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub> was also recorded; at our low temperature limit of -70 °C, the Re-*H* had begun to collapse to a broad hump but coalescence was not achieved. The  $^{31}P{^{1}H}$  NMR spectra of Re<sub>2</sub>H<sub>8</sub>(arphos)<sub>2</sub> and Re<sub>2</sub>H<sub>8</sub>(dppe)<sub>2</sub> are very similar with singlets at  $\delta$  + 57.0 and + 53.1 [7], respectively, for their solutions in C<sub>6</sub>D<sub>6</sub>. These chemical shifts are characteristic of five-membered rings formed by chelating phosphines bound to rhenium [9], so we believe that both Re<sub>2</sub>H<sub>8</sub>(arphos)<sub>2</sub> and Re<sub>2</sub>H<sub>8</sub>(dppe)<sub>2</sub> contain chelating arphos and dppe ligands and their formation from the  $\text{Re}_2\text{Cl}_4(\beta\text{-arphos})_2$  and  $\text{Re}_2\text{Cl}_4(\beta\text{-dppe})_2$  starting materials involves a switch in the bonding of the two arphos and dppe ligands from an intramolecular bridging mode in the chloro complexes [10] to a chelating mode in the dirhenium octahydrides.

The solid state structures of  $\text{Re}_2\text{H}_8(\text{arphos})_2$  and  $\text{Re}_2\text{H}_8(\text{dppe})_2$  are probably best represented as  $\text{Re}_2(\mu-H)_4\text{H}_4(\text{LL})_2$  (LL = arphos or dppe) by analogy with the structures determined for other octahydrides of this type [7,11,12]. Our attempts to obtain single crystals of  $\text{Re}_2\text{H}_8(\text{arphos})_2$  for a single crystal X-ray structure analysis were unsuccessful. Orange crystals of *trans*-[ReO<sub>2</sub>-(arphos)\_2]ReO\_4 were isolated during the crystal growing

process. A full data set was collected, but the structure was not refined because this complex was found to be isostructural with *trans*-[ReO<sub>2</sub>(dppe)<sub>2</sub>]ReO<sub>4</sub> which had been isolated and structurally characterized during our earlier attempts to grow single crystals of Re<sub>2</sub>H<sub>8</sub>(dppe)<sub>2</sub> [13]. These observations reflect the sensitivity of both complexes to small amounts of oxygen during the rather long crystal growing process.

The complex  $Re_2H_8(arphos)_2$  constitutes one of several octahydrododirhenium-arsine complexes which are now known. In addition to  $Re_2H_8(AsPh_3)_4$  [14,15], mixed phosphine-arsine complexes of the !ypes  $Re_2H_8$ -( $PR_2Ph$ )<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub> and  $Re_2H_8(PRPh_2)_3(AsPh_3)$  (R = Me or Et) are easily prepared and have been characterized [15], as have triphenylstibine complexes of these same types [15] and  $Re_2H_6(SPh_3)_5$  [46]. Accordingly, arsine (and stibine) ligands readily stabilize rhenium polyhydrides to give complexes which, at least in the case of the octahydridodirhenium species, have comparable stabilities to their all-phosphine analogues.

While there is indeed a relative paucity of arsine complexes of mononuclear rhenium polyhydrides [1], we have experienced little difficulty in preparing such complexes which contain the arphos ligand. In addition to the previously reported isomers ReH<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>( $\eta^1$ -arphos–As) and ReH<sub>5</sub>-(PPh<sub>3</sub>)<sub>2</sub>( $\eta^1$ -arphos–P), as well as the analogous complex ReH<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>( $\eta^1$ -dpae) (where dpae = Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>-AsPh<sub>2</sub>) [17], we have now prepared ReH<sub>7</sub>(arphos) in moderate yield by the reaction of ReOCl<sub>3</sub>(arphos) with NaBH<sub>4</sub> in ethanol. Control of the reaction temperature is critical, since above room temperature significant quantities of dinclear Re<sub>2</sub>H<sub>8</sub>(arphos)<sub>2</sub> are formed following loss of H<sub>2</sub> from ReH<sub>7</sub>(arphos).

The CV of a solution of ReH<sub>7</sub>(arphos) in 0.1 M TBAH– CH<sub>2</sub>Cl<sub>2</sub> displays an irreversible oxidation at  $E_{p,a} = +1.54$  V versus Ag/AgCl, a process which is similar to that seen in the CVs of other heptahydridorhenium complexes [18]. The Nujol mull IR spectrum of ReH<sub>7</sub>(arphos) exhibits quite strong  $\nu$ (Re–H) modes at 1994, 1960 and 1894 cm<sup>-1</sup>. Although we have not been able to determine the crystal structure of ReH<sub>7</sub>(arphos), it may well be structurally similar to that of ReH<sub>7</sub>(dppe) which is best described as a classical polyhydride in the solid state with a distorted tricapped trigonal prismatic geometry [19].

The <sup>1</sup>H NMR spectrum of ReH<sub>7</sub>(arphos) in CD<sub>2</sub>Cl<sub>2</sub> displays a doublet for the Re-*H* resonance at  $\delta - 6.74$  (<sup>2</sup>*J*(P-H) = 13.4 Hz), signifying that the molecule is fluxional in solution and that seven equivalent hydride ligands are coupled to the single P atom of the arphos ligand. For the analogous complex ReH<sub>7</sub>(dppe), the Re-*H* resonance is a binomial triplet at  $\delta - 6.64$  (<sup>2</sup>*J*(P-H) = 18.6 Hz) in CD<sub>2</sub>Cl<sub>2</sub>; this resonance is at  $\delta - 5.74$  in C<sub>6</sub>D<sub>6</sub>. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of CD<sub>2</sub>Cl<sub>2</sub> solutions of ReH<sub>7</sub>(arphos) and ReH<sub>7</sub>

(dppe) consist of singlets at  $\delta$  +46.4 and +42.9, respectively, in accord with chelating arphos and dppc ligands [9].

Loza and Crabtree [1] have noted that  $ReH_7(AsPh_3)_2$  is remarkably stable and surprisingly unreactive towards several reagents which react easily with ReH<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub>. It has already been established that  $\operatorname{ReH}_7(\operatorname{dppe})$  is appreciably more stable than  $\text{ReH}_7(\text{PPh}_3)_2$  in its thermal chemistry [5,20]. Preliminary experiments have indicated that  $\operatorname{ReH}_7(\operatorname{arphos})$  is in turn much less reactive than  $\operatorname{ReH}_7(\operatorname{dppe})$ . Thus, while  $\operatorname{ReH}_7(\operatorname{PPh}_3)_2$  reacts quite rapidly with a chelating organic acid such as pyridine-2-carboxylic acid (Hpic) to afford ReH(pic)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in high yield [21], the comparable reaction with ReH<sub>7</sub>(dppe) requires 3 days [22], while with ReH<sub>7</sub>(arphos) no significant reaction occurs even after 5 days. To what extent this difference in reactivity of ReH<sub>7</sub>(arphos) and ReH<sub>7</sub>(dppe) reflects differences in the nature of the Re-H bonding in these two complexes is unclear at present.

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