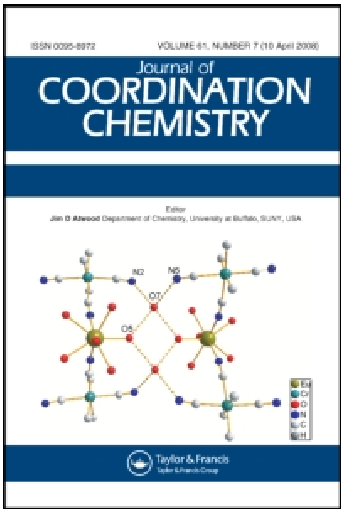

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Rhenium(VII) polyhydrides supported by chelating <i>bis</i> -phosphine ligands: DPEphos, xantphos and biphep

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Rhenium(VII) polyhydrides supported by chelating *bis*-phosphine ligands: DPEphos, xantphos and biphep

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Three new rhenium polyhydride complexes, [$ReH_7(L_2)$], incorporating bidentate organophosphorus ligands (L_2 = DPEphos, xantphos and biphep), were successfully synthesized using the corresponding [$ReOCl_3(L_2)$] complexes as precursors. The polyhydride complexes were characterized by IR, ^1H and ^{31}P NMR, and elemental analysis.

Keywords: Rhenium; Polyhydrides; Synthesis; Large bite-angle phosphines

1. Introduction

Transition metal hydrides are a fascinating family of compounds with a wide variety of useful and interesting properties, playing a role in homogeneous catalysis [1–3], exhibiting novel hydrogen bonding behavior [4–7], and having unique structural properties [8–11]. These complexes have been implicated as intermediates in a variety of reactions, such as hydrogenation and hydroformylation [12–15], and can be found in biological systems, such as nickel-dependent hydrogenase enzymes [16], and in industry [17]. The discovery of the dihydrogen bond ($M–H \cdots H–X$, where M = transition metal or boron; X = N, O, F) has reinvigorated the field of hydride chemistry [4, 5]. Metal complexes that exhibit dihydrogen bonding can have important roles in reactions such as proton transfer and σ-bond metathesis [7]. Since hydrides are intermediates in a number of catalytic reactions, the synthesis and characterization of such complexes can lead to design and development of more efficient catalysts. A thorough understanding of the properties of hydride complexes [18–22] is central to both understanding the current applications and the development of new synthetic protocols.

Transition metal polyhydrides, such as $[ReH_9]^{2-}$, [$ReH_7(PPh_3)_2$] and [$IrH_5(PPh_3)_2$], are usually high-coordination number complexes having three or more hydride ligands, in addition to other supporting ligands [23]. Hydride complexes can be classified into three structural types, depending upon the strength of the H–H and M–H

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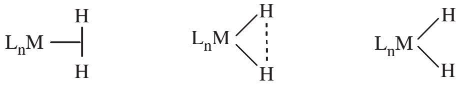
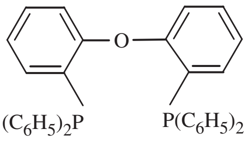
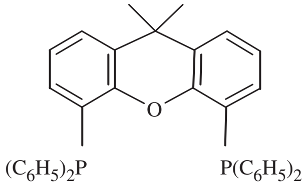


Non-classical Stretched Classical

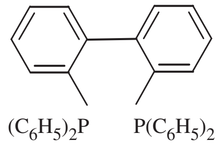
Figure 1. Hydride classification; M = transition metal, L = ligands, n = 5–7.



DPEphos



Xantphos



Biphep

Figure 2. Diphosphine ligands.

interactions: non-classical, stretched, and classical (figure 1) [24]. The nature of the supporting ligand influences the structure of the complex, specifically with respect to the interactions between the hydride ligands attached to the metal center. For example, the utility of wide bite-angle diphosphines in the synthesis of ruthenium dihydrogen complexes gave hydride complexes of the type *cis*-$[RuH_2(diphosphine)_2]$, which upon protonation resulted in dihydrogen complexes, *cis*-$[RuH(H_2)(diphosphine)_2]^+$ [25]. The bulk of the diphosphine ligands leads to a *cis* configuration which allows for intramolecular exchange of the hydrogens. The thermal instability of these complexes, where H_2 loss occurs at 233 K, may be explained by the smaller π-back-bonding available due to the geometric constraints of the wide bite-angle diphosphines [25].

We report here the synthesis and characterization of three new rhenium polyhydride complexes comprising diphosphines of varying bite-angle: DPEphos, xantphos, and biphep (bite-angle range, $\beta_n \sim 100\text{–}110^\circ$) using six-coordinate complexes of rhenium containing chloro, oxo, and diphosphine ligands [26] (figure 2), $[ReOCl_3(L_2)]$, as the hydride precursors.

2. Experimental

2.1. *Materials and methods*

Anhydrous solvents (methylene chloride, diethyl ether, tetrahydrofuran, and hexanes), lithium aluminum hydride, and celite were obtained from Aldrich. Phosphines were purchased from Strem. All reagents were used as received. Anhydrous sodium sulfate was obtained from Fisher. The polyhydride complexes were prepared using an adaptation of the literature method [18]. All manipulations were carried out using standard Schlenk techniques under an argon atmosphere.

Variable temperature nuclear magnetic resonance spectroscopy was carried out on a Bruker 500 MHz instrument. The T_1 values were obtained at various temperatures with a 400 MHz Varian Mercury spectrometer equipped with a BB *z*-axis gradient probe utilizing a 180-τ-90 pulse sequence. Proton spectra were measured in deuterated methylene chloride and referenced internally using the residual solvent protons as a reference. The ^{31}P NMR spectra were referenced externally to 85% phosphoric acid. All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were obtained on a Mattson Genesis Series FTIR using mulls on sodium chloride plates.

2.2. *Synthesis of rhenium(VII) polyhydride complexes (1–3)*

To a 100 mL Schlenk flask, 1.0007 g (1.1810 mmol) of [$ReOCl_3$(DPEphos)] was added, followed by 30 mL of diethyl ether. The resulting turquoise-green slurry was cooled in an ice bath prior to the addition of 10 equivalents of lithium aluminum hydride (0.4007 g, 10.56 mmol). After 4 h at room temperature, the greenish-grey slurry was filtered through celite to obtain a yellow solution. The solvent was removed *in vacuo* and cold THF (25 mL) was added via cannula. This solution was slowly quenched with water (0.18 mL in 10 mL THF) and dried with anhydrous sodium sulfate. The resulting slurry was filtered through celite and the volume of the solvent reduced *in vacuo*. Hexanes (25 mL) was added to precipitate an off-white solid which was dried and stored under argon. Yield of [ReH_7(DPEphos)] (**1**): 414 mg (48%). Anal. Calcd for $C_{36}H_{35}OP_2Re \cdot 2H_2O$ (%): C, 56.30; H, 5.13. Found: C, 55.85; H, 5.15. IR (Nujol): $\nu_{Re–H}$ 1935 and 1956 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.52–6.50 (m, 28H, aromatic H), $\delta - 5.60$ (t, 7H, $^2J_{PH} = 14$ Hz, Re–H), T_1 min = 61 ms (223 K, 400 MHz). ^{31}P NMR (CD_2Cl_2): δ 8.27 (s). Selectively hydride coupled ^{31}P NMR: δ 8.42 (octet, $^2J_{PH} = 14$ Hz).

A similar procedure was followed for **2** and **3**. Yield of [ReH_7(xantphos)] (**2**): 148 mg (18%). Anal. Calcd for $C_{39}H_{39}OP_2Re \cdot H_2O$ (%): C, 60.68; H, 5.10. Found: C, 61.53; H, 4.27. IR (Nujol): $\nu_{Re–H}$ 1990, 1968, and 1939 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.51–6.14 (br m, 26H, aromatic H), δ 1.71 (s, 6H, -CH_3 groups), $\delta - 5.62$ (t, 7H, $^2J_{PH} = 15$ Hz, Re–H), $T_1 = 87$ ms (233 K, 400 MHz). ^{31}P NMR (CD_2Cl_2): δ 2.17 (s). Yield of [ReH_7(biphep)] (**3**): 552 mg (62%). Anal. Calcd. for $C_{36}H_{35}P_2Re \cdot H_2O$ (%): C, 58.91; H, 5.09. Found: C, 58.93; H, 4.92. IR (Nujol): $\nu_{Re–H}$ 1948 and 1918 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.81–6.55 (br m, 28H, aromatic H), $\delta - 5.72$ (t, 7H, $^2J_{PH} = 14$ Hz, Re–H), $T_1 = 96$ ms (203 K, 400 MHz). ^{31}P NMR (CD_2Cl_2): δ 15.61 (s).

3. Results and discussion

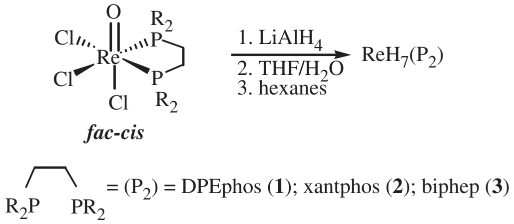
3.1. *Synthesis*

The rhenium(V) precursors, [ReOCl$_3$(L$_2$)], react with lithium aluminum hydride to form polyhydride complexes **1**–**3**, [ReH$_7$(L$_2$)] (scheme 1). The complexes are air-sensitive solids that have spectroscopic properties consistent with known [ReH$_7$(L$_2$)] complexes [27, 28]. The phosphines (figure 2) were chosen in order to vary the steric parameters (bite-angle range, $\beta \sim 100$–110°) of the ligand set. Variation in the yields for these complexes may reflect difficulty in the formation of the rhenium-alumino-hydride intermediate as a result of the steric interference of the supporting diphosphine. The most rigid diphosphine in this study, xantphos, gave the lowest yield (18%) compared to biphep (62%) and DPEphos (48%).

3.2. *Spectroscopic characterization of (1–3)*

Complexes **1**–**3** contain rhenium(VII) centers which are formally d^0 systems. The phosphorus resonance for **1**, at δ 8.27, has shifted from $\delta - 31.0$, the phosphorus resonance for the d^2 precursor [ReOCl$_3$(DPEphos)]. The phosphorus resonances for polyhydride complexes **2** and **3** are δ 2.17 and 16.6, respectively, whereas the phosphorus resonances for the precursors of **2** and **3** are found at $\delta - 36.6$ and -20.4 (dd, $J = 12$ Hz), respectively. A single phosphorus resonance is observed for all of the polyhydride complexes due to the fluxionality typical for complexes of higher coordination numbers (table 1) [22].

At room temperature, the proton NMR of **1** shows a set of multiplets centered at δ 7.01 due to the aromatic protons on the ligand backbone and a triplet resonance at δ −5.60 due to the hydride ligands. This was corroborated by a selectively hydride coupled ^{31}P NMR spectrum, showing an octet at δ 8.42 which confirms the presence of



Scheme 1. Synthesis of ReH$_7$P$_2$ complexes.

Table 1. Spectroscopic data for **1**–**3**.

Complex	**1**	**2**	**3**
$\nu_{\text{Re–H}}$(cm^{-1}) (nujol mull)	1935, 1956	1990, 1968, 1939	1948, 1918
^{1}H NMR(ppm)^a (CD$_2$Cl$_2$)	−5.60 (t, $J_{\text{PH}} = 14$ Hz)	−5.62 (t, $J_{\text{PH}} = 15$ Hz)	−5.72 t, $J_{\text{PH}} = 14$ Hz)
^{31}P NMR(ppm)^b (CD$_2$Cl$_2$)	8.27	2.17	16.6

Notes: $^a\delta$ Re–H only; t = triplet.
^{b}Referenced externally to 85% H$_3$PO$_4$.

seven equivalent hydride ligands. For compound **2**, the aromatic protons are found in the region between δ 7.51 and 6.14 and the hydride resonance is found at δ – 5.62 (t, $J_{PH} = 15$ Hz). The aromatic protons of the coordinated biphep ligand in complex **3** are found in the region between δ 7.81 and 6.93 and the hydride resonance is found at δ – 5.72 (t, $J_{PH} = 14$ Hz).

The variable temperature ^{1}H NMR data for **1** shows first decoalescence at approximately 213 K, while for **2** similar decoalescence starts at 233 K and only one of the two broad features present at 213 K resolves into a triplet at 193 K (figure 3). This deceleration of the fluxional process observed for **2** relative to **1** may reflect the increased rigidity of the xantphos backbone, which causes a reduction in the number of degrees of freedom available to the complex. For **3**, however, the triplet resonance at δ – 5.72 just begins to broaden at 193 K, which is evidence of a higher degree of fluxionality for this complex, compared to **1** and **2**. Based on the variable temperature NMR studies and comparison with previously published data [26], it is likely that these complexes adopt a tricapped trigonal prismatic geometry with the phosphines occupying the eclipsed prism positions (figure 4).

Variable temperature proton NMR spectroscopy was also utilized to determine the minimum T_1 values for each complex in order to attempt to ascertain the classical or non-classical nature of the hydride ligands [27]. For **1**, a minimum T_1 value of 61 ms

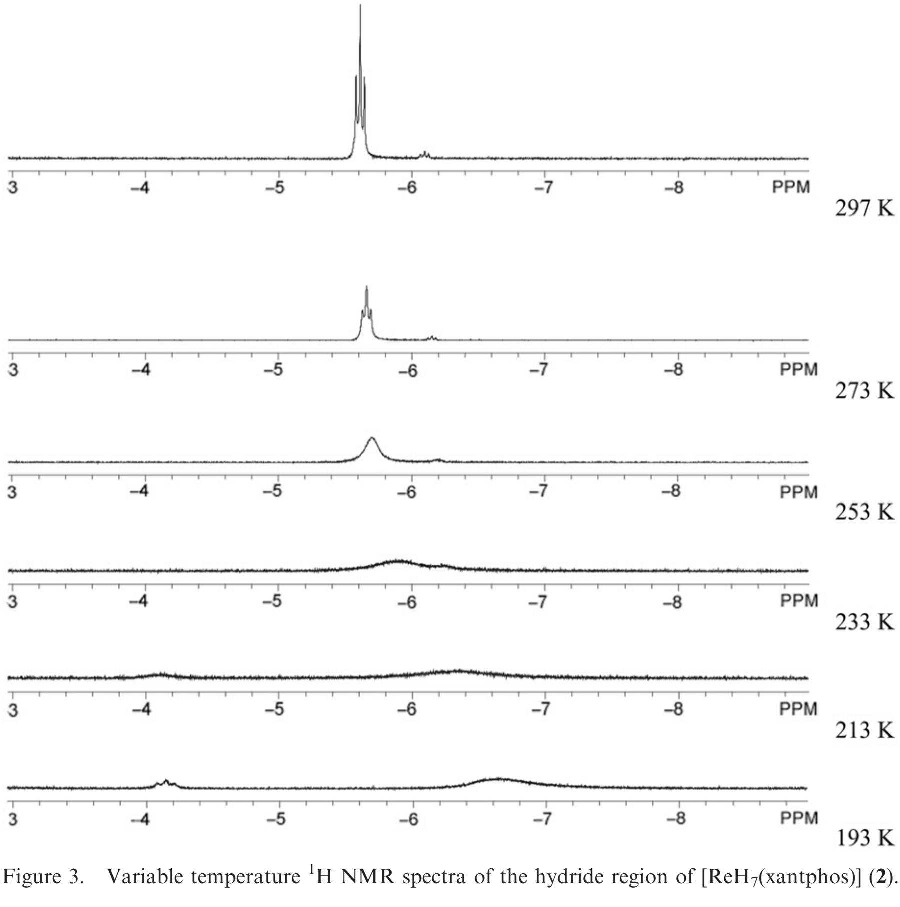
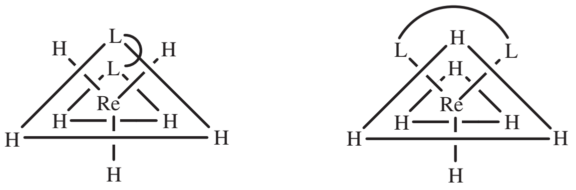


Figure 3. Variable temperature ^{1}H NMR spectra of the hydride region of [ReH$_7$(xantphos)] (**2**).



eclipsed prism equatorial capping

Figure 4. Possible conformations for $[ReH_7(L_2)]$ complexes.

was observed at 223 K, which is strongly suggestive of a classical structure in solution. For **2** and **3**, we were unable to obtain a minimum T_1 value, as T_1 continued to decrease throughout the temperature range in which the complex is soluble. The lowest T_1 value obtained for **2** was 87 ms at 233 K, again suggestive of a classical structure in solution. A T_1 value of 96 ms for **3** obtained at 203 K is again suggestive of a classical structure in solution. It is perhaps noteworthy that **1**, having the phosphine with the largest β_n value of this set, shows a smaller value of T_1. This would seem to be consistent with the idea that a larger bite-angle leads to a more sterically demanding ligand, which may help to compress the coordination sphere available to the hydride ligands and thus increase their proximity to each other [11].

The weak Re–H stretches in the infra-red spectra for these complexes are all found in the region 1900–2000 cm^{-1}, well within the range observed for classical polyhydride systems [20]. A correlation between bite-angle and metal-hydride stretch was not readily apparent.

4. Conclusions

We have found that Re(VII) polyhydride complexes supported by large bite-angle chelating diphosphines can be formed from $[ReOCl_3(L_2)]$ precursors. These complexes exhibit fluxional behavior at room temperature, similar to other polyhydride complexes, and most likely adopt a classical tricapped trigonal prismatic structure. The activity of these complexes in hydrogen transfer reactions is currently under investigation.

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