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$[\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3]^-$: The First Member of a New Class of Anionic Polyhydride Dimers $[Re_2H_7L_4]^-$

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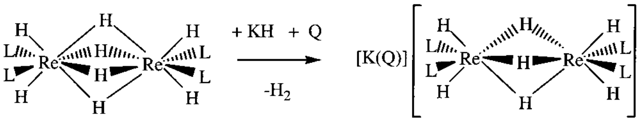
A variety of monomeric, anionic rhenium hydride salts are known, and they have been conveniently synthesized by the deprotonation of neutral polyhydride complexes by use of a strong base, such as KH.[1−4] The anionic complexes are of interest as they have been shown to display a wide range of basicities[4] and, in the presence of a hydrogen bond donor source, they have also been shown to form extended structures held together by protonic−hydridic bonds[5,6] (also referred to as dihydrogen bonds[7]). To date, the only examples of anionic dirhenium polyhydride complexes (greater than two hydrides[8]) reported are $[(H)_6Re(\mu\text{-}H)_3Re(CH_3C(CH_2P(C_6H_5)_2)_3)]^-$ [9,10] and $[(CO)_3Re(\mu\text{-}H)_3Re(CO)_3]^-$.[11] The former unsymmetrical dimer was prepared by the reaction of ReH_9^{2-} with triphos and was shown to contain three bridging hydrides. A few heteronuclear dimers are also known: $[(H)_3(PPh_3)_2Re(\mu\text{-}H)_3M(CO)_3)]^-$, M = Cr, Mo, W[12,13] and $[(H)_3(PPh_3)_2Re(\mu\text{-}H)_3U(C_5Me_5)_2Cl)]^-$.[14] Here we report the synthesis and characterization of $[K(Q)][\{Re_2H_2(PMePh_2)_2\}_2(\mu\text{-}H)_3]$ (Q = 18-crown-6 or 1,10-diaza-18-crown-6), the first members of a novel series of anionic dirhenium polyhydride salts of the form $[\{Re_2H_2(L)_2\}_2(\mu\text{-}H)_3]^-$.[15] These have been prepared by a one step deprotonation reaction of the neutral conjugate acid $\{ReH_2(L)_2\}_2(\mu\text{-}H)_4$, using KH in the presence of the appropriate crown ether (Scheme 1).

The neutral rhenium polyhydride dimeric precursors (**1**) are well known and can be conveniently prepared by elimination of H_2 from the monomeric heptahydride complexes, $ReH_7(L)_2$ (L = PPh_3, $PMePh_2$, $PEtPh_2$).[16,17] An alternative preparation involves hydride addition to $Re_2Cl_4(L)_4$ (L = PMe_3, PEt_3, P^nPr_3, $PMePh_2$, $PEtPh_2$, and PMe_2Ph) complexes.[18,19] In this study, $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ is conveniently prepared by a two step process.[20] The first step is the addition of hydride to $ReCl_4(PMePh_2)_2$,[21] by use of $LiAlH_4$, to form $ReH_7(PMePh_2)_2$. The second step is similar to the one reported by Chatt and Coffey,[16] and it involves heating $ReH_7(PMePh_2)_2$ to 68 °C under Ar in an EtOH/THF (3:1) solution to convert it to the $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ complex.

Scheme 1



(1) **(2)**

The neutral dimer reacts with 1 equiv of KH in the presence of a crown-ether in THF to yield $[K(Q)][\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3]$ (**2**) as a red, air-sensitive, crystalline salt.[22] The ^1H NMR spectrum of the salt at room temperature shows a characteristically broad singlet at −8.42 ppm due to a rapid exchange of terminal and bridging hydrides. A singlet in the $^{31}P\{^1H\}$ NMR spectrum at 19.03 ppm is consistent with four equivalent phosphines. The variable temperature ^1H NMR spectra in the hydride region of $[K(1,10\text{-diaza-18-crown-6})][\{ReH_2(PMePh_2\}_2(\mu\text{-}H)_3]$ in THF-d_8 were recorded. At −20 °C the peak decoalesces, and at −64 °C two hydride resonances are detected in a 3:4 intensity ratio, indicative of four terminal hydrides ($\delta = -9.42$, t, $J = 7.5$ Hz, 4H) and three bridging hydrides ($\delta = -7.46$, br, 3H). The solid-state infrared spectrum shows two terminal ReH vibrational modes, at 1935 and 1892 cm^{-1}.

Complex **1** in THF at 20 °C was shown to be in equilibrium with the acid $OP(OEt)_2NHPh$ (**4**), with $\mathrm{p}K_\alpha^{\mathrm{THF}} = 32 \pm 4$[4] (Scheme 2) and with an equilibrium constant of $K_{eq} = 0.079$. The $\mathrm{p}K_\alpha^{\mathrm{THF}}$

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(20) Diethyl ether (15 mL) was added to a mixture of $ReCl_4(PMePh_2)_2$ (0.950 g, 1.30 mmol) and $LiAlH_4$ (0.30 g, 7.9 mmol) under Ar and the reaction mixture was stirred for 3 h. It was then was filtered, and ethanol (15 mL) was added dropwise to the filtrate over a period of 2.5 h. The solvent was then removed under vacuum, and the resulting brown powder was shown by ^1H NMR to be $ReH_7(PMePh_2)_2$. This was dissolved in 20 mL of THF/ethanol (1:3) and refluxed for 4 h under Ar. $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ precipitated as a bright red solid and was washed with EtOH (3 × 8 mL). Yield: 0.354 g, 46.0%. ^1H NMR (benzene-d_6): 7.68−7.57 (m, 16 H, C_6H_5), 6.98−6.86 (m, 24 H, C_6H_5), 1.80 (d, 12H, $^2J(PH) = 8.7$ Hz, PCH_3), −5.85 (quin, 8H, $^2J(PH) = 9.0$ Hz, ReH). ^{31}P NMR(benzene-d_6): 14.97 (s).

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(22) Typical procedure conducted under Ar: THF (5 mL) was added to a mixture of $Re_2H_8(PMePh_2)_4$ (72 mg, 0.061 mmol), 1,10-diaza-18-crown-6 (16 mg, 0.061 mmol), and KH (8 mg, 0.20 mmol), and was stirred for 8 h. Excess KH was filtered from the solution and washed with THF (3 mL). The combined filtrate was evaporated to dryness to yield a dark red crystalline powder which was recrystallized from THF/diethyl ether. Yield: 50 mg (55%). ^1H NMR (THF-d_8): 7.76−7.07 (m, 40 H, C_6H_5), 3.63 (m, 16 H, CH_2), 2.74 (m, 8 H, CH_2), 1.65 (qnt, 2 H, NH), 1.89 (d, $^2J(PH) = 7.5$ Hz, PCH_3), −8.42 (br, 7H, ReH). $^{31}P\{^1H\}$ NMR (THF-d_8): 19.03 (s). IR (neat):ν_{Re-H} 1935 (s), 1892 (s); ν_{NH} 3292 (w), 3231 (br) cm^{-1}.

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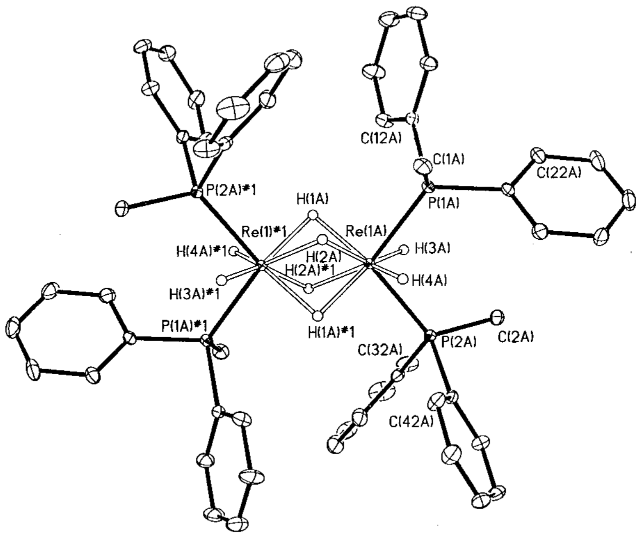

Figure 1. The structure of $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ in molecule A of two independent molecules. Selected bond lengths (Å) and angles (deg): Re(1A)−Re(1A)#1 2.5338(2), Re(1A)−H(4A) 1.55(4), Re(1A)−H(3A) 1.57(4), Re(1A)−H(2A) 1.68(4), Re(1A)−H(2A)#1 1.93 (4), Re(1A)−H(1A) 1.84 (4), Re(1A)−H(1A)#1 1.77(4), Re(1A)−P(1A) 2.3351(8), Re(1A)−P(2A) 2.3503(9). H(4A)−Re(1A)−H(3A) 119(2), H(4A)−Re(1A)−H(2A) 78(2), H(3A)−Re(1A)−H(2A) 147(2), H(4A)−Re(1A)−H(1A)#1 86(2), H(3A)−Re(1A)−H(1A)#1 137(2), H(2A)−Re(1A)−H(1A)#1 66(2).

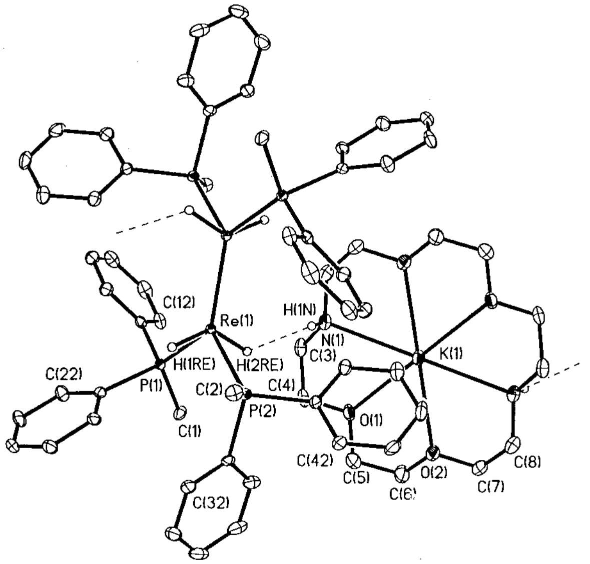

Figure 2. The structure of [K(1,10-diaza-18-crown-6)][$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3$]. Selected bond lengths (Å) and angles (deg): Re(1)−H(1Re) 1.51(3), Re(1)−H(2Re) 1.54(4), Re(1)−P(2) 2.3131(8), Re(1)−P(1) 2.3137(7), Re(1)−Re(1)#1 2.5958(2). H(1Re)−Re(1)−H(2Re) 137(2), H(1Re)−Re(1)−P(2) 72(1), H(2Re)−Re(1)−P(2) 77(1), H(1Re)−Re(1)−P(1) 82(1), H(2Re)−Re(1)−Re(1)#1 109(1), H(2Re)−Re(1)−Re(1)#1 113(1).

Scheme 2

$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ + [K(2,2,2-crypt)][$OP(OEt)_2NPh$] $\rightleftharpoons$
1 **3**

[K(2,2,2-crypt)][$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3$] + $OP(OEt)_2NHPh$
2 **4**

(the approximate free-ion pK_a)[23] for $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ was calculated to be 33 ± 4 by using eq 1 and an estimate of the difference in ion pair dissociation constants $\Delta pK_d = 0.4$.[24]

$$pK_\alpha^{THF}(\mathbf{1}) = pK_\alpha^{THF}(\mathbf{4}) - pK_{eq} + \Delta pK_d \tag{1}$$

The structures of $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ and [K(1,10-diaza-18-crown-6)][$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3$], as determined by single-crystal X-ray crystallography, are shown in Figures 1 and 2, respectively.[25] Both structures have a center of inversion midway between the two rhenium atoms. The Re−Re distance in $\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_4$ is 2.5338(2) Å, which is similar to those of the $\{ReH_2(L)_2\}_2(\mu\text{-}H)_4$ complexes that have been studied previously by single-crystal X-ray and neutron diffraction.[26] [K(1,10-diaza-18-crown-6)]$^+$[$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3$]$^-$ crystallizes with the phosphines eclipsed across a Re−Re bond distance of 2.5958(2) Å. This Re−Re bond distance is significantly longer than that determined for the neutral conjugate acid, but is similar to the 2.594(1) Å Re−Re bond distance for (μ-H)$_3$ bridged complex [NEt_4][$Re_2(\mu\text{-}H)_3H_6(CH_3C(CH_2P(C_6H_5)_2)_3)$].[10] The extended structure of [K(1,10-diaza-18-crown-6)][$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H)_3$], as determined by X-ray diffraction, consists of chains held together by protonic hydridic bonds, with NH···HRe distances of about 2.2 Å between the terminal ReH and the NH. This distance was calculated by correcting the observed N−H distance, 0.77(4) Å, to the 1.0 Å NH distance that is typically determined by neutron diffraction methods, thus shortening the observed H···H distance of 2.35 Å to approximately 2.2 Å. The terminal hydrides were located and refined isotropically, with Re−H distances of 1.51(3) and 1.54(4) Å, however, the bridging hydrides were not located. Attempts to obtain X-ray quality crystals of the 18-crown-6 analogue without the protonic hydridic interaction have not been successful to date, thus illustrating the utility of using azacrowns and protonic-hydridic bonding in crystallization.

Further work will examine the effect of the ligand L in the dimers [$Re_2H_7L_4$]$^-$ on the hydrogen bond accepting ability and the basicity of these anions, as measured by the pK_α^{THF} value of the conjugate acid $Re_2H_8L_4$. Initial studies show that analogous anionic dimers, with other phosphine ligands such as $P(p\text{-}C_6H_4F)_3$ and PMe_3, can be prepared.[15]

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Supporting Information Available: X-ray crystallographic files, in CIF and PDF format, for $C_{52}H_{60}P_4Re_2$ and $C_{64}H_{86}KN_2O_6P_4Re_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) pK_α^{THF} is an approximation to the absolute free ion pK_α^{THF} value, which is obtained by crudely correcting the observed K for 1:1 ion pairing effects by use of the Fuoss equation (see ref 4).

(24) The correction for ion pairing ΔpK_d (see ref 4 for an explanation of this correction) was calculated using the ionic radius of [K(2,2,2-crypt)]$^+$ (5 Å), of [$OP(OEt)_2NPh$]$^-$ (3 Å), and of [$\{ReH_2(PMePh_2)_2\}_2(\mu\text{-}H_3)$]$^-$ (4.3 Å) (determined from the distance between K and the midpoint of the Re−Re bond).

(25) Crystals of [K(1,10-diaza-18-crown-6)][$\{ReH_2(PMePh)_2\}_2(\mu\text{-}H_3)$] suitable for X-ray analysis were grown by slow diffusion of hexane into a THF solution of the salt. Crystallographic data for $C_{64}H_{86}KN_2O_6P_4Re_2$: a = 11.0535(2), b = 12.157(1), c = 13.2904(3) Å, α = 66.782(1)°, β = 74.983(1)°, γ = 83.151(1)°, with Z = 1 in space group P1. V = 1584.91(5) Å^3, T = 150(1) K, D_{calc} = 1.553 mg/m^3, R1(F) [$I > 2\sigma(I)$] = 0.0260, wR2 [all data] = 0.0624, and data/restraints/parameters = 7250/0/364. Crystals of $\{ReH_2(PMePh_2)_2\}(\mu\text{-}H)_4$ suitable for X-ray analysis were grown by slow diffusion of hexane into a THF solution of the compound. Crystallographic data for $C_{52}H_{60}P_4Re_2$: a = 9.2683(1), b = 13.3189(2), c = 19.4136(4) Å, α = 89.148(1)°, β = 84.436(1)°, γ = 87.011°, with Z = 2 in space group $P\bar{1}$. V = 2381.83(7) Å^3, T = 150(1) K, D_{calc} = 1.647 mg/m^3, R1(F) [$I > 2\sigma(I)$] = 0.0301, wR2 [all data] = 0.0720, and data/restraints/parameters = 13768/0/560.

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