$[Re_2(\mu\text{-}H)_3H_4\{CH_3C(CH_2PPh_2)_3\}]^-$, the First Example of an $M{\equiv}MH_7$ Co-ordination Sphere

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The complex $Et_4N[Re_2H_7\{MeC(CH_2PPh_2)_3\}]{\cdot}MeCN$, prepared by reacting $(Et_4N)_2ReH_9$ and $MeC(CH_2PPh_2)_3$ in acetonitrile, is shown to contain the $Re_2(\mu\text{-}H)_3$ group with the Re atoms linked by a $\sigma^2\pi_{\parallel}{}^2\pi_{\perp}{}^2$ triple bond and with the ligand phosphorus atoms co-ordinated to one Re atom while four terminal hydride ligands complete a distorted pentagonal bipyramid of H atoms about the second Re atom.

A new compound, $Et_4N[Re_2H_7(triphos)]$ [triphos = $MeC(CH_2PPh_2)_3$], containing a rhenium atom co-ordinated to four terminal hydrogen atoms and linked to a second rhenium atom by three hydride bridges and a triple bond, is described in this communication. The complex is the first in which a metal atom serves as the only nonhydride ligand bonded to a second metal atom co-ordinated by hydrogen.

The complex $Et_4N[Re_2H_7(triphos)]$ was prepared† by adding $(Et_4N)_2ReH_9$[1] (550 mg, 1.2 mmol) to a solution of triphos (750 mg, 1.2 mmol) in acetonitrile (150 ml). After refluxing for 10 min, the red solution was left at room temperature for 2 days. The solvent was removed *in vacuo* leaving a red semi-solid. Extraction of the residue with 1:2 propan-2-ol–diethyl ether left behind a yellowish–orange powder which, upon crystallization from $MeCN–Et_2O$, gave a red crystalline air-sensitive product {200 mg, 28%; m.p. 119 °C decomp. Elemental analysis corresponded to $[Et_4N][Re_2H_7(triphos)]{\cdot}MeCN$}. A 200 MHz ^1H n.m.r. spectrum of the complex in CD_3CN at ambient temperature shows a high-field singlet at τ 15.62 ($w_{\frac{1}{2}}$, 11 Hz) which is assigned to Re–H. Integration of the high-field line with respect to $-CH_2N$ (τ 6.84, quartet) gives H/Re = 7.1. The 300 MHz ^{31}P n.m.r. spectrum under similar conditions is also a singlet. A sharp i.r. peak at 2245 cm^{-1} confirms the presence of lattice acetonitrile.

N.m.r. equivalence of the Re–H in $[Re_2H_7(triphos)]^-$ is attributed to nonrigid stereochemistry, a ubiquitous property of high co-ordination number rhenium hydride complexes.[2] The absence of coupling in the n.m.r spectrum indicates that the P and terminal H atoms are co-ordinated to different Re atoms. Bridging Re–H often fails to give observable phosphorus–hydrogen coupling.[3]

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† The synthesis and all subsequent manipulations were conducted under argon or helium atmospheres. Solvents were distilled under nitrogen.

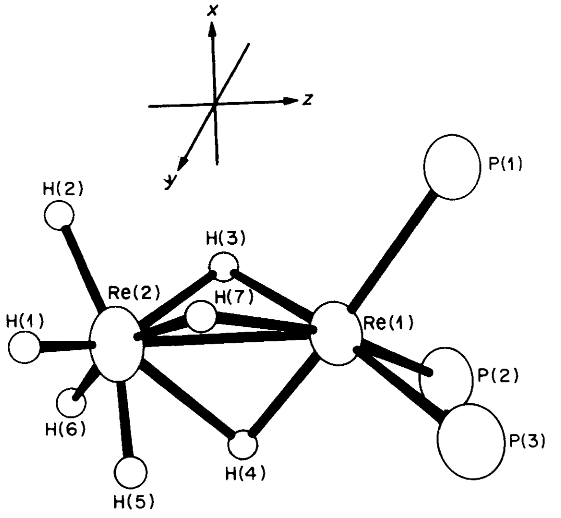

Figure 1. Perspective view of the $[Re_2H_7(triphos)]^-$ anion, omitting the organic part of the phosphine ligand. The origin of the co-ordinate system for the $X\alpha$ calculation was at the centre of the Re–Re bond; the yz-plane is the symmetry plane.

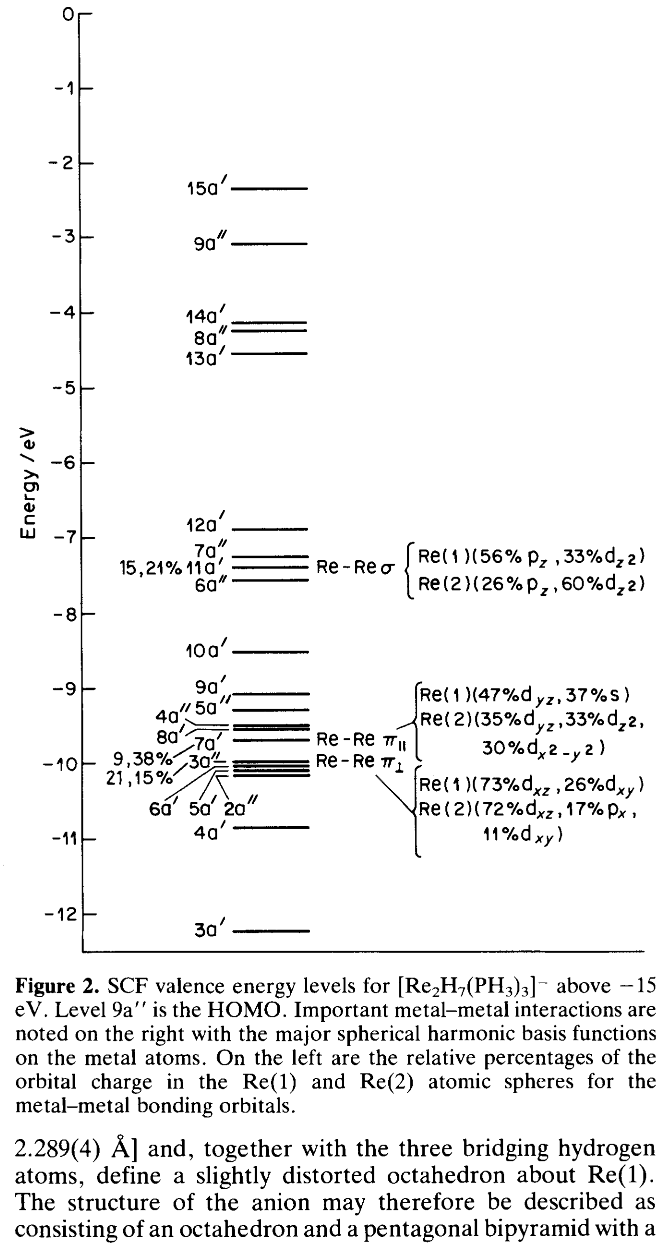

Figure 2. SCF valence energy levels for $[Re_2H_7(PH_3)_3]^-$ above −15 eV. Level 9a″ is the HOMO. Important metal–metal interactions are noted on the right with the major spherical harmonic basis functions on the metal atoms. On the left are the relative percentages of the orbital charge in the Re(1) and Re(2) atomic spheres for the metal–metal bonding orbitals.

The structure of $Et_4N[Re_2H_7(triphos)]\cdot MeCN$ was determined by X-ray diffraction from an epoxy-coated ground spherical crystal. Solution and refinement of the crystal structure shows that the dinuclear anion has the atomic arrangement shown in Figure 1.‡ The two Re atoms are separated by 2.597(1) Å and are bridged by three hydrogen atoms with average bridging distances for Re(1)–H and Re(2)–H of 1.85(7) and 1.77(20) Å respectively. Within the relatively large errors, the three hydrogen bridges form an equilateral triangle with edge lengths H(3)–H(4) 2.12(10), H(4)–H(7) 2.17(10), and H(7)–H(3) 2.28(10) Å. The remaining four hydride ligands are co-ordinated to Re(2) in terminal positions at an average distance of 1.59(14) Å. Together, the terminal and bridging hydrogen atoms define a distorted pentagonal bipyramid about Re(2). The H(6) and H(7) hydrogens are in the apical positions [H(6)–Re(2)–H(7) 159°] while the equatorial plane is defined by H(1)–H(2)–H(3)–H(4)–H(5) [maximum deviation from the mean plane 0.28(10) Å for H(1)]. Re(1) caps the H(3)–H(4)–H(7) face of the pentagonal bipyramid. The three phosphorus atoms of the triphos molecule are linked to Re(1) [mean Re–P distance 2.289(4) Å] and, together with the three bridging hydrogen atoms, define a slightly distorted octahedron about Re(1). The structure of the anion may therefore be described as consisting of an octahedron and a pentagonal bipyramid with a common triangular face of H atoms.

The geometry of the $[Re_2H_7(triphos)]^-$ anion is similar to that reported[4] for the molecule $[Re_2H_4L_4L'_2]$ [L = PMe_2Ph, L′ = $P(OCH_2)_3CEt$] in which an $L_2L'Re(\mu\text{-}H)_3$ octahedron and an $L_2L'HRe(\mu\text{-}H)_3$ pentagonal bipyramid share a triangular face. The Re–H, Re–P, and Re–Re distances in $[Re_2H_7(triphos)]^-$ are in agreement with the values reported for $[Re_2(\mu\text{-}H)_3HL_4L'_2]$,[4] $[Re_2(\mu\text{-}H)_3H_2L_4L'_2]^+$,[4] $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CNBu^t)_2]^+$,[3] and $[Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4]$.[5] Electron counting and assumption of the 18-electron rule predicts a Re–Re quadruple bond for $[Re_2H_7(triphos)]^-$ and triple bonds for the other complexes cited. In comparison to non-hydrogen bridged Re–Re bond lengths, the hydrogen bridged distances are similar to a Re–Re double bond and much longer than quadruple or triple bonds.§

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‡ *Crystal data* (295 K): a = 12.384(3), b = 11.582(3), c = 19.323(4) Å, α = 101.89(2), β = 94.80(2), γ = 109.53(2)°, U = 2520.8 Å^3, Z = 2, D_x = 1.549 g cm^{-3}, triclinic, space group $P\bar{1}$. All 6376 reflections with $(\sin\theta)/\lambda \leqslant 0.42$ Å^{-1} were measured and corrected for Lorentz, polarization, absorption, and linear decline effects, resulting in 2565 independent observations with $F_m > 3\sigma(F_m)$: the internal agreement factor R_{int} 0.0122 was based on 2411 pairs of equivalent [$F(hkl)$ and $F(\overline{hkl})$] reflections. No evidence for primary or secondary extinction was detected. Based on a combination of Patterson and direct methods followed by Fourier series and least-squares, all non-hydrogen atoms were located and refined with anisotropic thermal parameters except for one carbon atom of the disordered solvate molecule. The seven H atoms bonded to Re(2) and the six methylene H atoms in the $MeC(CH_2PPh_2)_3$ group, determined from the difference Fourier series, were refined with isotropic thermal parameters. The final agreement factors are R = 0.0236, R_w = 0.0363, S = 1.633. Refinement of the H atom positions and thermal motion was possible because of the accurate diffraction measurements. The atomic co-ordinates for this work are available on request from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by a full literature citation for this communication.

§ Compare the following Re–Re distances from ref. 6: unbridged $\sigma^2\pi^4\delta^2$ bond in $Re_2Cl_6(PEt_3)_2$, 2.22 Å; unbridged $\sigma^2\pi^4\delta^2\delta^{*2}$ bond in $Re_2Cl_4(PEt_3)_4$, 2.22 Å; 1-Cl bridged $\sigma^2\pi^2$ bond in Re_3Cl_9, 2.49 Å. The unbridged single bond in $(C_5H_5)_2Re_2(CO)_5$ has an Re–Re distance of 2.96 Å.

The nature of the Re–Re bond in $[Re_2H_7(triphos)]^-$ has been elucidated by relativistic self-consistent field $X\alpha$-scattered wave calculations on the C_s model complex $[Re_2(\mu\text{-}H)_3H_4(PH_3)_3]^-$.¶ The spin-restricted calculations were made as previously described;[7] the results are summarized in Figure 2. Important Re–Re interactions occur only in levels 11a′(Re–Re σ bonding), 7a′ (in-plane Re–Re π bonding), and 3a″ (out-of-plane Re–Re π bonding) (Figure 2). The unusual situation of having the metal–metal π bonding orbitals at lower energy than the metal–metal σ-bonding orbital is a consquence of strong Re–H bonding components in levels 7a′ and 3a″. In addition to the Re–Re σ and π bonding interactions, there is a very weak δ bonding interaction in level 8a″ which is cancelled by a δ* interaction in level 9a″. The $X\alpha$ analysis therefore shows that the metal–metal bond in $[Re_2H_7(triphos)]^-$ is best described as a $\sigma^2\pi_{\parallel}{}^2\pi_{\perp}{}^2$ triple bond. The bond is relatively weak because all the Re–Re bonding orbitals also have strong bonding components with H or P atoms, which results in a reduction of the charge in the Re–Re bonding component.

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¶ The Re–H, Re–P, and Re–Re bond lengths in the model were experimental values for the triphos complex. The dihedral angles between the Re(1)–H_{br}–Re(2) planes were idealized to 120°. Other minor adjustments were made in bond angles to make H(1), H(2), H(3), H(4), and H(5) exactly coplanar, and to make H(1), H(6), H(7), Re(1), Re(2), and P(2) lie in a mirror plane: the experimental atomic positions for these atoms do not differ appreciably from C_s symmetry.

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