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Conversion of $Re_2H_4(dppe)_3$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to Its Conjugate Acid $[Re_2H_5(dppe)_3]^+$ Involving the Switch in Coordination Mode of a dppe Ligand from Chelating to Bridging

The important isomerization process that leads to the conversion of multiply bonded complexes of the type α-$M_2X_4(dppe)_2$ (M = Mo, W; X = Cl, Br; dppe = $Ph_2PCH_2CH_2PPh_2$) to β-$M_2X_4(dppe)_2$ involves a switch in the bonding mode of *both* dppe ligands from chelating to bridging, with an associated change in rotational geometry about the M–M bond from eclipsed to staggered.[1,2] During our examination of the reactivity of the dirhenium octahydride complex $Re_2H_8(dppe)_2$ (**1**),[3] we have found that it reacts with dppe to give the tetrahydride complex $Re_2H_4(dppe)_3$ (**2**), which is readily protonated to afford salts of the type $[Re_2H_5(dppe)_3]X$ (**3**). This conversion, which is itself very uncommon,[4,5] is accompanied by an unexpected change in the bonding mode of *one* of the dppe ligands from chelating to bridging.

The reaction between **1** (0.19 g, 0.16 mmol) and dppe (0.14 g, 0.36 mmol) in THF (15 mL) for 17 h afforded an orange solution. This was treated with methanol (30 mL) and the volume of the solution reduced by evaporation to produce **2** as a red-brown precipitate. This was filtered off, washed sparingly with methanol and diethyl ether, and then dried under vacuum; yield 0.20 g (78%).[6] The conversion of **2** into $[Re_2H_5(dppe)_3]BF_4$ (**3a**) was accomplished by adding $HBF_4 \cdot Et_2O$ (0.06 mL) to a solution of **2** (0.055 g, 0.035 mmol) in dichloromethane (2 mL). Addition of diethyl ether (30 mL) to the dark green solution produced a gray-green precipitate of **3a**; yield 0.05 g (84%).[6]

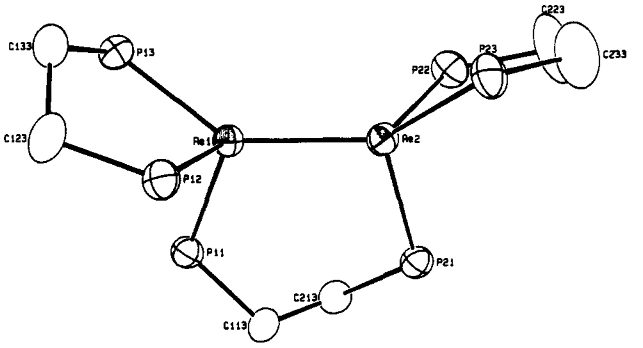
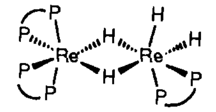


Figure 1. ORTEP view of the structure of the $[Re_2H_5(dppe)_3]^+$ cation of **3b** with the phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level. The positions of the bridging and terminal hydrido ligands were not determined. Some representative bond lengths (Å) and angles (deg) are as follows: Re–Re = 2.576 (1), Re(1)–P(11) = 2.336 (3), Re(1)–P(12) = 2.391 (3), Re(1)–P(13) = 2.373 (3), Re(2)–P(21) = 2.360 (3), Re(2)–P(22) = 2.334 (3), Re(2)–P(23) = 2.361 (3); Re(2)–Re(1)–P(11) = 108.61 (8), Re(2)–Re(1)–P(12) = 115.66 (8), Re(2)–Re(1)–P(13) = 140.97 (8), Re(1)–Re(2)–P(21) = 105.27 (8), Re(1)–Re(2)–P(22) = 124.92 (9), Re(1)–Re(2)–P(23) = 130.24 (9), P(11)–Re(1)–P(12) = 94.7 (1), P(11)–Re(1)–P(13) = 105.5 (1), P(12)–Re(1)–P(13) = 79.3 (1), P(21)–Re(2)–P(22) = 94.4 (1), P(21)–Re(2)–P(23) = 115.6 (1), P(22)–Re(2)–P(23) = 80.1 (1). The P(11)–Re(1)–Re(2)–P(21) torsional angle (χ) involving the bridging dppe ligand is 8.0 (1)°.

The ^1H NMR spectrum of the neutral complex $Re_2H_4(dppe)_3$ was examined over a temperature range (in C_6D_6 from +70 to +20 °C and in CD_2Cl_2 from +30 to −70 °C). At the low-temperature limit of −70 °C, the hydride resonances appear as two broad singlets of similar intensity at δ −4.3 and −11.4. As the temperature is raised, these resonances broaden slowly (and shift slightly) until coalescence is reached (by ca. +70 °C). The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **2** (in CD_2Cl_2) exhibits broad resonances at δ +49.2 and +46.9, the former being the much broader of the two. As the temperature is lowered to −70 °C, these resonances shift downfield slightly. The peak at δ +46.9 shifts to δ +49.4 but otherwise remains essentially unchanged, while the other splits into two sharper resonances at δ +52.9 and +52.4.[7] The three resonances seen at −70 °C are of similar intensity, thereby suggesting the presence of three pairs of inequivalent phosphorus atoms. Since the chemical shifts of these phosphorus resonances are characteristic of *chelating* dppe ligands in dirhenium complexes,[8] we favor I as representing the



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[1] (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 1.

[2] (a) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99. (b) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801. (c) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1984**, *23*, 3383. (d) Cole, N. F.; Derringer, D. R.; Fiore, E. A.; Knoechel, D. J.; Schmitt, R. K.; Smith, T. J. *Inorg. Chem.* **1985**, *24*, 1978. (e) Agaskar, P. A.; Cotton, F. A.; Derringer, D. R.; Powell, G. L.; Root, D. R.; Smith, T. J. *Inorg. Chem.* **1985**, *24*, 2786. (f) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1986**, *25*, 15.

[3] Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 395.

[4] We know of only one previous example of the conversion of a complex of the type $Re_2H_4L_6$ (L = phosphine) into its conjugate acid $[Re_2H_5L_6]^+$. This has been reported for the mixed phosphine–phosphite complex $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$.[5]

[5] Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.

[6] Elemental microanalytical data are as follows. Anal. Calcd for $C_{78}H_{76}P_6Re_2$ (**2**): C, 59.60; H, 4.88. Found: C, 59.21; H, 5.21. Calcd for $C_{79}H_{79}BCl_2F_4P_6Re_2$ (i.e. $[Re_2H_5(dppe)_3]BF_4 \cdot CH_2Cl_2$ (**3**)): C, 54.39; H, 4.57. Found: C, 54.70; H, 4.54.

[7] The downfield shift of these resonances with a decrease in temperature may reflect the presence of a small amount of paramagnetic impurity, probably $[Re_2H_4(dppe)_3]^+$. This species is readily produced by the one-electron oxidation of **2** ($E_{1/2}$ = −0.54 V vs Ag/AgCl in 0.1 M TBAH–CH_2Cl_2).

[8] Anderson, L. B.; Bakir, M.; Walton, R. A. *Polyhedron* **1987**, *6*, 1483.

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most likely structure of **2**. This structure also accords with the ^1H NMR spectrum (vide supra), which shows resonances attributable to bridging and terminal Re–H units at δ −4.3 and −11.4, respectively.

The protonation of **2** by $HBF_4 \cdot Et_2O$ to give **3a** is irreversible as evidenced by our failure to deprotonate **3a** with the use of NEt_3, KH, $LiEt_3BH$, *n*-BuLi, or KO-*t*-Bu. This suggests that a major structural difference exists between **2** and **3a**, a conclusion supported by a single-crystal X-ray structure determination and by NMR spectroscopy.

Single crystals of **3a** and its perrhenate analogue $[Re_2H_5(dppe)_3]ReO_4$ (**3b**) were subjected to X-ray structure determinations.[9] The refinement of the structure of **3a** was taken to the stage where its isostructural relationship to **3b** could be unambiguously established.[10] However, since our attempts to refine the anion (and some lattice solvent molecules that were present in the crystals of **3a**) proved not to be entirely satisfactory, the refinement was not continued. The key features of the structure of the $[Re_2H_5(dppe)_3]^+$ cation in **3b** (hydride ligands were not located) are shown in Figure 1.[11-14] There are two chelating and one bridging dppe ligands, a situation different from that proposed in the case of **2** (three chelating dppe ligands). Especially interesting is the observation that the two chelate rings have quite different conformations. The ring formed at Re(2) has an "envelope"-type puckering[15] with the P–C–C–P unit being almost planar (torsional angle of ca. 5 (2)°). The other ring is much more puckered as shown by the P(13)–C(133)–C(123)–P(12) torsional angle of ca. 49 (1)°. The dirhenium cation possesses no crystallographically imposed symmetry. The Re–Re distance of 2.576 (1) Å in the $[Re_2H_5(dppe)_2(\mu\text{-dppe})]^+$ cation is slightly shorter than those distances reported for the analogous phosphite $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$ (2.605 (2) Å)[5] and isocyanide $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ (2.604 (1) Å)[16] complexes, and is characteristic of hydrido-bridged metal–metal-bonded dirhenium complexes. The average Re–P distance of 2.359 (3) Å is also consistent with those found in these structures.[5,16] While we did not locate the hydride ligands in this structure determination, the presence of three bridging hydride ligands and one terminal hydride per rhenium atom is compatible with the geometry of the Re_2P_6 skeleton as defined in Figure 1.

The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **3a** (in CD_2Cl_2) exhibits two singlets at δ +59.4 and +22.7 (intensity ratio 2:1), the chemical shifts of which are characteristic of chelating and bridging dppe ligands, respectively.[8] When this solution is cooled to −40 °C, the downfield signal splits out into singlets of equal intensity at δ +62.6 and +58.6, signifying the presence of inequivalent pairs of phosphorus atoms associated with the chelating dppe ligands. This is consistent with the very low symmetry of the structure as shown in Figure 1. At this same temperature (−40 °C), the ^1H NMR spectrum (in CD_2Cl_2) shows a bridging hydride resonance at δ −6.6 (broad singlet) and an apparent quartet at δ −7.7 with the correct relative intensities, the latter feature being assigned to the terminal hydride ligands that are each coupled to three phosphorus atoms ($^2J_{PH} \simeq 37$ Hz). When this solution is allowed to warm to +30 °C, these resonances coalesce and transform into a broad singlet at δ −7.3. The ^1H NMR spectrum of a solution of this complex in CD_3NO_2 shows that between +30 and +70 °C this singlet remains essentially unchanged.

The isolation of **2** and its subsequent protonation to give **3** provides only the second example of a dirhenium tetrahydride/pentahydride conjugate pair. The unusual structural change that accompanies the conversion of **2** to **3**, namely, the switch of a single chelating dppe ligand to an *intramolecular* bridging mode, suggests that unusual structural rearrangements may be exhibited by other bidentate and polydentate phosphine complexes of the dirhenium polyhydrides.[17] Studies along these lines are currently under way, including the synthesis and characterization of mixed-phosphine complexes such as $Re_2H_4(dppe)_2(\mu\text{-dppm})$.

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Supplementary Material Available: A listing of atomic positional parameters for the structure of $[Re_2H_5(dppe)_3]ReO_4$ (4 pages). Ordering information is given on any current masthead page.

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(9) Crystals of **3a** were grown from CH_2Cl_2/n-heptane, while **3b** was obtained serendipitously during attempts to grow crystals of $Re_2H_8(dppe)_2$ (**1**) from THF/methanol over a period of several weeks. Apparently, a portion of **1** decomposed with release of dppe, which then reacted with **1** to produce $[Re_2H_5(dppe)_3]^+$. The formation of the $[ReO_4]^-$ anion can be attributed to the slow diffusion of oxygen into the system during the prolonged period over which these reactions and subsequent crystal growth occurred. The presence of $[ReO_4]^-$ was confirmed by IR spectroscopy (ν(ReO) $\simeq$ 905 (s) cm^{-1}).

(10) Structural parameters for the $[Re_2H_5(dppe)_3]^+$ cation in **3a** and **3b** are identical within experimental error. Data for **3a** are available upon request from R.A.W.

(11) Dark orange crystals of **3b** are monoclinic, space group $P2_1/n$, with $a = 12.177$ (1) Å, $b = 23.152$ (2) Å, $c = 26.843$ (4) Å, $\beta = 100.32$ (1)°, $V = 7445$ (3) $Å^3$, $Z = 4$, $d_{calcd} = 1.477$ g/cm^3. X-ray data were collected at 21 °C on a 0.45 × 0.26 × 0.17 mm crystal for 9988 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius diffractometer using graphite-crystal-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection and reduction methods are the same as described elsewhere.[12] An empirical absorption correction was applied,[13] but no correction for extinction was made. The Re, P, and C atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[14] The hydride ligands and the oxygen atoms of the perrhenate anion did not refine satisfactorily. Hydrogen atoms of the phenyl groups were not included in the refinement. The perrhenate rhenium atoms were located in two general positions and refined to multiplicities of 76% (Re(3)) and 24% (Re(4)) when constrained to have a multiplicity $M_{Re(3)} = 100 - M_{Re(4)}$. The final residuals were $R = 0.048$ ($R_w = 0.060$) for 5923 data with $I > 3.0\sigma(I)$.

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(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(14) (a) Cromer, D. T. In *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974, Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. In *Ibid.*; Table 2.2B.

(15) This "envelope"-type puckering has been encountered previously with dimetal complexes that contain dppe and related bidentate phosphine ligands. See, for example: Bakir, M.; Cotton, F. A.; Falvello, L. R.; Vidyasagar, K.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2460.

(16) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.

(17) An interesting example of an unsymmetrical complex that contains the tridentate phosphine ligand triphos has been encountered in the anionic species $[H_6Re(\mu\text{-}H)_3Re(triphos)]^-$ (triphos = $CH_3C(CH_2PPh_2)_3$), which has been prepared from the reaction of $[ReH_9]^{2-}$ with triphos: Abrahams, S. C.; Ginsberg, A. P.; Koetzle, T. F.; Marsh, P.; Sprinkle, C. R. *Inorg. Chem.* **1986**, *25*, 2500.