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One-pot synthesis and the X-ray structures of rhenium(I) diphosphine hydrides, *fac*-(CO)₃(P–P)ReH [P–P = dppp, dppb, and dppfe]

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Abstract

The reactions of $\text{Re}_2(\text{CO})_{10}$ with chelated diphosphines, P–P, where P–P are 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), and 1,1'-bis(diphenylphosphino)ferrocene (dppfe), in refluxed 1-pentanol or 1-hexanol afford the corresponding hydrides 1–3 *fac*-(CO)₃(P–P)ReH, (for 1, P–P is dppp, for 2, P–P is dppb, and for 3, P–P is dppfe) in high yield. The hydrides 1–3 have been characterized spectroscopically and by X-ray crystal structure determinations. © 2004 Elsevier B.V. All rights reserved.

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Rhenium(I) tricarbonyl-diphosphine hydrides, *fac*-(CO)₃(P–P)ReH, (L–L = diphosphine) are of interest because they serve as starting materials for the synthesis of a wide variety of organometallic compounds [1–7]. It is, therefore, important to find out an easy method of synthesis of rhenium(I) tricarbonyl-diphosphine hydrides, *fac*-(CO)₃(P–P)ReH. A general method of synthesis of rhenium(I) tricarbonyl-diphosphine hydrides is to treat rhenium pentacarbonyl hydride with the corresponding diphosphines, P–P, as shown in Eq. (1) [8,9]:

$$(CO)_5 ReH + P - P \rightarrow (CO)_3 (P - P)ReH + 2CO$$
 (1)

However, the synthesis of $(CO)_5$ ReH is a long and tedious process, involves special glassware or equipment, requires extensive vacuum-line manipulations, and is a two-step process as shown in Eqs. (2) and (3) [10,11]:

$$\operatorname{Re}_{2}(\operatorname{CO})_{10} + 2\operatorname{Na} \to 2[(\operatorname{CO})_{5}\operatorname{Re}]\operatorname{Na}$$
(2)

$$[(CO)_5 Re]Na + H_3 PO_4 \rightarrow (CO)_5 ReH + [H_2 PO_4]Na$$
(3)

 $(CO)_5ReH$ was also prepared from the reaction of zinc and acetic acid with $Re(CO)_5Br$ [12]. The later was obtained from the reaction of $Re_2(CO)_{10}$ with liquid bromine [13]. Here, we report a relatively easy one-pot synthesis and X-ray structures of the rhenium(I) tricarbonyl-diphosphine hydrides, *fac*-(CO)₃(dppp)ReH (1), *fac*-(CO)₃(dppb)ReH (2), and *fac*-(CO)₃(dppfe)ReH (3), where, dppp is 1,3-bis(diphenylphosphino)propane, dppb is 1,4-bis(diphenylphosphino)butane, dppfe is 1,1'-bis(diphenylphosphino)ferrocene.

Reaction of $\text{Re}_2(\text{CO})_{10}$ with diphosphines, P–P in 1pentanol produces the hydrides, 1–3 in high yield [14]. Similar reaction of $\text{Re}_2(\text{CO})_{10}$ with triphenylphosphine for several days yielded an unidentified compound, rather than the expected hydride, *cis*-(CO)₄(PPh₃)ReH

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[9]. We did not attempt to identify this unknown compound at this time. Therefore, the present method of synthesis of the diphosphine hydrides 1-3 cannot be applied for the synthesis of analogous monophosphine hydrides, *cis*-(CO)₄(PPh₃)ReH. The diphosphine hydrides, 1-3 have been characterized spectroscopically. The IR spectrum of each exhibits three strong $v(C \equiv O)$'s in the region 2015–1915 cm⁻¹, characteristic of facial geometry [9]. Similar $v(C \equiv O)$'s were also observed in the IR spectrum of *fac*-(CO)₃(dppe)ReH [9]. The ¹H NMR spectrum of each shows a very high field resonance as triplet in the region δ –4.0 to –5.0, due to the hydride



Fig. 1. The X-ray crystal structure of fac-(CO)₃(dppp)ReH (1). Selected bond lengths (Å): Re(1)–C(1), 1.949(5); Re(1)–C(2), 1.941(4); Re(1)–P(1), 2.4497(9); Re(1)–H(1), 1.70(4). Selected bond angles (°): O(1)–C(1)–Re(1), 178.4(5); O(2)–C(2)–Re(1), 179.1(3); C(1)–Re(1)–H(1), 171 (2); C(2)#–Re(1)–P(1), 171.75(11); P(1)–Re(1)–H(1), 78.0(10); C(2)–Re(1)–H(1), 94.1(11); C(3)–P(1)–Re(1), 116.10(11); C(5)–P(1)–Re(1), 116.00(12); C(11)–P(1)–Re(1), 115.31(13).



Fig. 2. The X-ray crystal structure of *fac*-(CO)₃(dppb)ReH (2). Selected bond lengths (Å): Re(1)–C(1), 1.948(5); Re(1)–C(2), 1.921(5); Re(1)–C(3), 1.946(5); Re(1)–P(1), 2.4603(12); Re(1)–P(2), 2.4268(11); Re(1)–H(1), 1.75(4). Selected bond angles (°): O(1)–C(1)–Re(1), 176.1(.4); O(2)–C(2)–Re(1), 178.9(5); O(3)–C(3)–Re(1), 176.7(4); C(1)–Re(1)–H(1), 173.6(14); C(2)–Re(1)–P(1), 172.0(2); C(3)–Re(1)–P(2), 168.6(2); P(1)–Re(1)–H(1), 78.7(14); P(2)–Re(1)–H(1), 77.6(14).



Fig. 3. The X-ray crystal structure of fac-(CO)₃(dppfe)ReH (**3**). Selected bond lengths (Å): Re(1)–C(1), 1.961(3); Re(1)–C(2), 1.925(4); Re(1)–C(3), 1.942(3); Re(1)–P(1), 2.4466(8); Re(1)–P(2), 2.4723(7); Re(1)–H(1), 1.78(3); Fe(1)···Re(1), 4.446(1); Fe(1)···H(1), 4.04(3). Selected bond angles (°): O(1)–C(1)–Re(1), 177.8(3); O(2)–C(2)–Re(1), 176.4(3); O(3)–C(3)–Re(1), 175.1(4); C(1)–Re(1)–H(1), 174.7(11); C(2)–Re(1)–P(1), 166.34(10); C(3)–Re(1)–P(2), 172.31(13); P(1)–Re(1)–H(1), 75.6(11); P(2)–Re(1)–H(1), 86.0(10).

coupled to the two phosphorus atoms. Similar high-field triplets were observed in related hydrido complexes [9]. The ¹³C NMR spectrum of each exhibits three low field resonances in the region δ 198–195 as three triplets due to three terminal CO's coupled to two phosphorus atoms. Finally, the three hydrides 1-3 were characterized through X-ray crystal structure determinations [15]. The molecular plots of 1-3 are shown in Figs. 1-3, respectively. As expected, the central rhenium atom of each is octahedrally coordinated to three terminal CO's in a facial arrangement, two phosphorus atoms of the chelated diphosphine, P-P, and the hydride ligand. Due to the expected low precision of the Re-H bond distance based on X-irradiation, the observed Re-H values in 1-3 tabulated below are all the same within three standard uncertainties, and are comparable to the value of 1.70(6) observed in mer-Re(CO)₃(PPh₂O-Me)H [16]. The displacement of the Re atom off of the equatorial plane is also comparable to the previous values observed in other octahedral Re(CO)₃(PR₃)₂H compounds [17]:

Distance (Å)	1	2	3
Re–H	1.70(4)	1.75(4)	1.78(3)
Re· · ·(P2C2)	0.154(2)	0.177(2)	0.165(1)

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 178949 for compound **1**, CCDC 178950 for compound **2**, and CCDC 178951 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

References

- M. Orchin, S.K. Mandal, J. Feldman, Inorg. Synth. 32 (1998) 300.
- [2] S.K. Mandal, D.M. Ho, M. Orchin, J. Organomet. Chem. 439 (1992) 53.
- [3] S.K. Mandal, J.A. Krause, M. Orchin, J. Organomet. Chem. 467 (1994) 113.
- [4] S.K. Mandal, D.M. Ho, M. Orchin, Inorg. Chem. 30 (1991) 2244.
- [5] M.T. Williams, C. McEachin, T.M. Becker, D.M. Ho, S.K. Mandal, J. Organomet. Chem. 599 (2000) 308.
- [6] S.K. Mandal, D.M. Ho, M. Orchin, Organometallics 12 (1993) 1714.
- [7] J. Cook, A. Hicks, T. Frazier, D.M. Kimari, T.A. Budzichowski, J.A. Krause Bauer, S.K. Mandal, J. Chem. Cryst. 33 (2003) 481.
- [8] S. Bolaño, J. Bravo, R. Carballo, S. García-Fontán, U. Abram, E.M. Vzquez-López, Polyhedron 18 (1999) 1431.
- [9] N. Flitcroft, J.M. Leach, F.J. Hopton, J. Inorg. Nucl. Chem. 32 (1970) 137.
- [10] P.S. Braterman, R.W. Harrill, H.D. Kaesz, J. Am. Chem. Soc. 89 (1967) 2851.
- [11] W. Beck, W. Hieber, G. Braun, Z. Anorg. Allg. Chem. 308 (1961) 23.
- [12] M.A. Urbancic, J.R. Shapley, Inorg. Synth. 28 (1990) 165.

- [13] S.P. Schmidt, W.C. trogler, F. Basolo, Inorg. Synth. 28 (1990) 162.
- [14] Synthesis of 1-3: In a typical experiment a mixture of about 2.5 mmol of Re₂(CO)₁₀ and 5.0 mmol of the corresponding P-P were refluxed in 100 mL of 1-pentanol for about 24 h. The mixture was allowed to cool to room temperature. At this time most of the hydride came out of the solution. The solid hydride was separated by filtration and kept aside. The filtrate was evaporated to dryness using a vacuum pump. The residue was dissolved in 50 ml of toluene. The toluene solution was passed through a silica gel column and evaporated to dryness. The residue and the solid hydride were combined together. The mixture was recrystallized from CH₂Cl₂-hexane at -5 °C. White crystals of 1 and 2 and orange crystals of 3 were collected by filtration. Data for 1: Yield, 91-93%. M.p. 209-210 °C (dec.). This hydride was characterized previously [13]. Data for 2: Yield, 81-85%. M.p. 225-228 °C. Anal. Calc. for C₃₁H₂₉O₃P₂Re: C, 53.3; H, 4.1. Found: C, 53.0; H, 4.1%. IR (Toluene, cm⁻¹): v(C=O) 2011s, 1930s, 1916s. ¹H NMR (CD₂Cl₂, δ , ppm): 7.55(m, 20H, C₆H₅), 2.26(m, 4H, CH₂CH₂CH₂CH₂), -4.61(t, J(PH) 25 Hz, H). ³¹P (CD₂Cl₂, reference: 85% H₃PO₄, δ , ppm): 7.44(s). ¹³C NMR (CD₂Cl₂, δ , ppm): 196.54(t, J (PC) 7 Hz, C=O), 195.83(t, J (PC) 19 Hz, C=O), 195.34(t, J (PC) 19 Hz, C=O), 139.25-128.75(m, C₆H₅), 32.79(t, J (PC) 14 Hz, -PCH₂-), 23.88(s, PCH₂CH₂-). Data for 3: Yield, 89-93%. M.p. 240- 244 °C (dec.). Anal. Calc. for $C_{37}H_{29}O_3P_2Re:$ C, 53.8; H, 3.6. Found: C, 53.6; H, 3.7%. IR (Toluene, cm⁻¹): v(C=O) 2012s, 1931s, 1921s. ¹H NMR (CD₂Cl₂, δ, ppm): 7.75(m, 20H, C₆H₅), 4.43(s, br, 1H, C₅H₄), 4.31(s, br, 1H, C5H4), 4.25(s, br, 1H, C5H4), 4.13(s, br, 1H, C5H4), -4.07(t, J (PH) 28 Hz, H). ³¹P (CD₂Cl₂, reference: 85% H₃PO₄, δ , ppm): 14.50(s). ¹³C NMR (CD₂Cl₂, δ , ppm): 197.04(t, J (PC) 7 Hz, C=O), 195.98(t, J (PC) 19 Hz, C=O), 195.44(t, J (PC) 21 Hz, C=O), 138.78/137.47(t, J (PC) 27/21 Hz, ipso, C₆H₅), 134.77/134.35(t, J (PC) 6/5 Hz, o, C₆H₅), 130.91/130.37(s, p, C₆H₅), 128.69/128.47(t, J (PC) 5/5 Hz, m, C₆H₅), 78.83-78.12(m, C₅H₄), 77.36(s, br, C₅H₄), 75.32(s, br, C₅H₄), 73.36(s, br, C₅H₄), 73.01(s, br, C₅H₄).
- [15] X-ray intensity data were collected on a Nonius Kappa CCD diffractometer and corrected for Lorentz-polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL (version 5.04). The non-hydrogen atoms were refined anisotropically. The hydrido ligand H(1) was located in a difference-Fourier map and its coordinates and isotropic displacement coefficient were also refined. The remaining H atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) and allowed to ride on their respective carbons. A dichloromethane solvent molecule was also located in both 1 and 3. Crystal data for 1: $C_{31}H_{29}Cl_2O_3P_2Re$, M = 768.62, colorless prisms, $0.29 \times 0.20 \times 0.12$ mm³, orthorhombic, space group Pnma (No. 62), a = 17.9160(5) Å, b = 21.6983(5) Å, c = 7.8031(2) Å, V = 3033.43(13) Å³, Z = 4, μ (Mo K α) = 4.318 mm⁻¹, scan mode (ω) = 0.5° × 800, θ range = 1.88–27.49°, 20874 reflections collected, 2968 ($I > 2\sigma I$) unique reflections were used in all calculations, number of variables = 215, R = 0.0275 (0.0600), $R_w =$ 0.0397 (0.0642), and goodness of fit = 1.043. Crystal data for 2: $C_{31}H_{29}O_3P_2Re$, M = 697.71, colorless prisms, $0.11 \times 0.10 \times 0.10$ mm³, triclinic, space group $P\bar{1} a = 15.9486(3)$ Å, b = 16.4544(3) Å, c = 11.0249(4) Å, V = 1514.62(5) Å³, Z = 2, μ (Mo K α) = 4.522 mm⁻¹, scan mode (ω) = 0.5° × 720, θ range = 1.92–27.49°, 38874 reflections collected, 4689 ($I > 2\sigma I$) unique reflections were used in all calculations, number of variables = 338, R = 0.0339 (0.0722), $R_w =$ 0.0565 (0.0820), and goodness of fit = 1.097. Crystal data for 3: $C_{38}H_{31}Cl_2FeO_3P_2Re$, M = 910.56, yellow plates, $0.10 \times 0.18 \times 0.18$ mm³, space group $P\bar{1}$ a = 10.0309(4) Å, b = 11.0249(4) Å, c = 17.8374(8) Å, $\alpha = 82.945(2)^{\circ}, \beta = 75.587(2)^{\circ}, \gamma = 84.389(2)^{\circ}, V =$ 1891.44(13) Å³, Z = 2, μ (Mo K α) = 3.840 mm⁻¹, scan mode $(\omega) = 1.0^{\circ} \times 500$, θ range = 1.18–27.51°, 17184 reflections collected, 7574 ($I > 2\sigma I$) unique reflections were used in all calculations, number of variables = 401, R = 0.0273 (0.0647), $R_w = 0.0331$ (0.0666), and goodness of fit = 1.055.
- [16] G. Albertin, S. Antoniutti, S. Garcia-Fontan, R. Carballo, F.J. Padoan, J. Chem. Soc., Dalton Trans. (1998) 2071.
- [17] U. FlÖrke, H.-J. Haupt, Zeit. Krist. 202 (1992) 317.