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The synthesis and reactions of Re^I carboxylic acids. The X-ray structure of *fac*-$Re(CO)_3(dppp)CO_2D \cdot 0.5C_6D_6$

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Abstract

The metallocarboxylic acids $Re(CO)_3(P-P)C(O)OH$ where (P–P) is either dppe [1,2-bis(diphenylphosphino)ethane] or dppp [1,3-bis(diphenylphosphino)propane] and their deuterio analogs have been prepared from the reaction of $[Re(CO)_4(P-P)]^+ BF_4^-$ with NaOH(D) and characterized. Concentrated benzene solutions of the dppp complex deposit the acid as a dimer with 1 mol of solvated benzene and the X-ray crystal structure study of the deuterio dimer acid is reported. The cationic salts, **1**, do not react with alcohols unless base is present. However, the acids are immediately esterified when they are dissolved in alcohols by virtue of the acids' spontaneous ionization through acyl-oxygen cleavage to the cation and hydroxyl anion; the latter abstracts a proton to give the conjugate base of the alcohol required for esterification. Solutions of the acids in DMSO undergo slow decarboxylation to the corresponding hydrides; addition of KOH to either DMSO or DMF solutions results in immediate decarboxylation.

Introduction

Organometal complexes possessing a carboxylic acid group sigma bonded to a transition metal, $M-CO_2H$, are of special interest for a number of reasons. They are postulated intermediates both in the Hg^{II} and Ag^1 aqueous solution oxidation of CO [1] as well as in the Fe (and other transition metal) carbonyl-catalyzed water–gas shift reaction [2]. In all these oxidation reactions, the putative carboxylic acid function spontaneously loses CO_2 to form the corresponding metal hydride. Furthermore these carboxylic acids, unlike conventional organic acids, may ionize [2c] by two different pathways:

$$M-CO_2^- + H^+ \rightleftharpoons M-C(O)OH \rightleftharpoons [M-CO]^+ + OH^-$$

The unusual acyl cleavage shown to the far right of the equilibria can be the exclusive mode of ionization [3] and hence some authors choose to characterize the metallocarboxylic acids as hydroxycarbonyl complexes. There are many reports on

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the synthesis of hydroxycarbonyl complexes of Fe [3,4], Ru [5], Re [6], Pt [7], and Ir [8] but such complexes are frequently difficult to isolate and purify and only recently has the first X-ray structure of one of them, *trans*-$Pt(Ph)(PEt_3)_2CO_2H$ been reported [7b]. We now report the preparation, characterization and some reactions of *fac*-$Re(CO)_3(P-P)CO_2H$ [where P–P is either 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane, (dppp)] as well as their deuterio analogs, one of which, *fac*-$Re(CO)_3(dppp)CO_2D$, has been subjected to X-ray analysis.

Results and discussion

Preparation and characterization

The Re hydroxycarbonyls and their deuterio analogs were prepared from the corresponding cations (**1a**, **b**) by reaction with NaOH(D) [6] in almost quantitative yield (eq. 1):

$$\underset{(1)}{[Re(CO)_4(P-P)]^+BF_4^-} + NaOX \rightarrow \underset{(2)}{fac\text{-}Re(CO)_3(P-P)C(O)OX} \qquad (1)$$

(1)	(2)
(**a**) P–P = dppe	(**a**) P–P = dppe; X = H
(**b**) P–P = dppp	(**b**) P–P = dppe; X = D
	(**c**) P–P = dppp; X = H
	(**d**) P–P = dppp; X = D

The starting BF_4 salts (**1a**, **b**) [9*] were prepared from the corresponding bromides by treatment with $AgBF_4$ and CO (see Experimental section). The elemental analyses, melting points and yields of new compounds are given in Table 1 and their spectroscopic data (IR, ^1H NMR and ^{13}C NMR) are given in Table 2. The complexes *fac*-$Re(CO)_3(P-P)Z$, where Z = C(O)OH, H, Br, all exhibit three strong terminal $\nu(CO)$ in the IR spectra characteristic of facial geometry [10*]. In nujol mulls in the IR spectra of the solid hydroxycarbonyls **2a**–**d** each show one $\nu(C{=}O)$ in the 1585–1565 cm^{-1} region. In benzene solution, the monomeric acids are in equilibrium with their dimers as evidenced by the presence of two carbonyl bands in the 1618–1575 cm^{-1} region. Such equilibria have been observed with other hydroxycarbonyls [7b,c]. Because the IR spectra of the protio complexes **2a** and **2c** did not show an OH band, the corresponding deuterio analogs **2b** and **2d** were prepared and these do exhibit weak bands at 2296 and 2272 cm^{-1}, respectively. The ^1H NMR spectra of the protio compounds **2a**, **2c** in C_6D_6 and CD_2Cl_2 did not show any resonances due to the OH protons but in dimethylsulfoxide (DMSO-d_6) low field resonances for these protons are observed at δ 9.29 and 9.80, respectively. Low field resonances due to OH protons in $Pt(C_6H_9)(P-P)C(O)OH$ were reported to be observed only in DMSO-d_6 [11]. The ^{13}C NMR spectra of **2a**, **2c** and **2d** all show a triplet between δ 201.6–199.0 assigned to the carboxyl carbon resonances.

The effect of solvents: decarboxylation

In DMSO solution our hydroxycarbonyls slowly (at room temperature for about 1 day) undergo decarboxylation to the corresponding hydrides (the dppp analog

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* Reference with asterisk indicates a note in the list of references.

Table 1

Elemental analyses [a], melting points and yields for compounds in the text

Compound	Elemental analyses			m.p. (°C)	Yield (%)
	Anal. calc. for	C (%)	H (%)		
1a	$C_{30}H_{24}BF_4O_4P_2Re$	45.9 (45.9)	3.2 (3.1)	275–276	89
1b	$C_{31}H_{26}BF_4O_4P_2Re$	46.3 (46.6)	3.2 (3.2)	210–211	93
2a	$C_{30}H_{25}O_5P_2Re \cdot CH_3CN$	50.7 (50.9)	3.6 (3.7)	159–160	94
2b	$C_{30}H_{26}O_5P_2Re$	50.1 (50.4)	3.6 (3.6)	162–163	95
2c	$C_{31}H_{27}O_5P_2Re$	51.1 (51.1)	3.8 (3.7)	149–151	94
2d	$C_{32}H_{28}O_5P_2Re \cdot CH_3CN$	51.3 (51.4)	3.8 (4.0)	150–153	96
3a	$C_{31}H_{27}O_5P_2Re \cdot 0.5C_6H_6$	53.4 (53.2)	4.0 (4.0)	147–148	35
3b	$C_{31}H_{28}O_5P_2Re \cdot 0.5C_6D_6$	53.5 (53.0)	3.8 (4.4)	153–154	41
4	$C_{30}H_{27}O_3P_2Re$	53.0 (52.7)	4.0 (4.0)	208–210	59
5	$C_{30}H_{26}BrO_3P_2Re$	47.2 (47.2)	3.5 (3.4)	> 260	95

[a] The numbers in parentheses correspond to the theoretical values.

takes somewhat longer). When a few drops of a 4 *M* aqueous solution of KOH is added to the DMSO or DMF solutions of the hydroxycarbonyl complexes, a transient deep yellow-orange color is observed and the corresponding hydrides *fac*-Re(CO)$_3$(P–P)H [12*] are formed almost immediately, precipitating as white solids on dilution with water. Obviously, the anion decarboxylates much more rapidly than the undissociated hydroxycarbonyl. The dppe acid and the dppp analog behave differently in benzene. When concentrated benzene solutions of the monomeric dppp complexes (**2c**, **d**) are left standing at room temperature, the hydroxycarbonyls precipitate as white crystals of the dimers, **3a**, **3b**, *fac*-[Re(CO)$_3$(dppp)CO$_2$H(D)]$_2$ · $C_6H_6(D_6)$, both of which are characterized spectroscopically. The X-ray crystal structure of the deuterio dimer acid, **3b**, is reported (*vide infra*). On the other hand, the dppe complexes (**2a**, **b**) on standing in benzene solution are slowly converted to the carbanato-bridged complex, *fac*-[Re(CO)$_3$(dppe)]$_2$(μ-O$_3$C). The characterization of this complex will be reported elsewhere. In *N*,*N*-dimethylformamide (DMF), the hydroxycarbonyls are moderately soluble. Contrary to the behavior reported for an FeCOOH species which ionizes completely to an FeCO$^+$ cation in this solvent [3], our hydroxycarbonyls hardly dissociate at all and after 1 or 2 days give only a trace of hydride; the major products are the carbanato-bridged complexes [Re(CO)$_3$(P–P)]$_2$(μ-O$_3$C) mentioned above. In methylene chloride solution, the hydroxycarbonyls slowly but only slightly ionize to the cation and OH$^-$ and such solutions are rather stable. If the solid hydroxycarbonyls are heated at about 110°C they slowly decarboxylate to the corresponding hydride.

Table 2

Spectral data for compounds in the text

Compound	IR (cm^{-1})[a]	^1H NMR (δ)[b]			^{13}C NMR (δ)[c]		
		C_6H_5	CH_2	Other	CO[d]	C_6H_5[e]	Other[f]
1a	2110s, 2029s,sh, 2017vs, 1999s, sh[g]	7.51 (m, 20H)	3.31 (m, 4H)				
1b	2109s, 2030s, 2007vs[g]	7.41 (m, 20H)	2.64 (m, 6H)				
2a	2023s, 1944s, 1925s, ν(C=O) 1618m, 1584w; ν(C=O) 1585m[h]	7.55 (m, 20H)	3.05 (m, 4H)	9.29 (s, 1H, OH), 2.49 (s, 3H, CH_3)	199.0 (t, 12 Hz, C=O), 195 (dd, 50 Hz, 11 Hz), 192.8 (t, 6 Hz)		25.1 (m) 118.2 (s, CN) 1.1 (s, CH_3)
2b	2023s, 1943s 1924s, ν(C=O) 1618m, 1573w; ν(C=O) 1572m, ν(O–D) 2296w[h]	7.57 (m, 20H)	3.05 (m, 4H)	2.48 (s, 3H, CH_3)			
2c	2027s, 1952s 1919s, ν(C=O) 1610m, 1573m; ν(C=O) 1567m[h]	7.50 (m, 20H)	2.40 (m, 6H)	9.80 (s, 1H, OH), 2.55 (s, 3H, CH_3)	201.7 (t, 11 Hz, C=O), 194.3 (t, 8 Hz), 192.8 (t, 19 Hz)		23.4 (t, 15 Hz); 19.6 (s) 118.2 (s, CN) 1.1 (s, CH_3)
2d	2028s, 1915s, 1919s, ν(C=O) 1609m, 1573m; ν(C=O) 1553m, ν(O–D) 2272w[h]	7.51 (m, 20H)	2.40 (m, 6H)	2.53 (s, 3H, CH_3)	201.6 (t, 11 Hz, C=O), 194.2 (t, 8 Hz), 192.7 (t, 18 Hz)		23.3 (t, 15 Hz, 195. (s), 118.2 (s, CN), 1.1 (s, CH_3)
3a	2013s, 1932s, 1920s, ν(C=O) 1574m[h]	7.55 (m, 23H)	2.43 (m, 6H)	9.87 (s, 1H, OH)			
3b	2022s, 1939s, 1914s; ν(C=O) 1578m[h]	7.58 (m, 20H)	2.40 (m, 6H)		201.7 (t, 11 Hz, C=O), 194.3 (t, 8 Hz), 192.8 (t, 18 Hz)		23.4 (t, 15 Hz), 19.6 (s), 128.6 (s, C_6D_6)
4	2011s, 1932s, 1913s	7.35 (m, 20H)	1.86 (m, 6H)	−4.07 (t, 26 Hz, H)	196.7 (t, 8 Hz), 195.0 (t, 17 Hz)		31.2 (t, 17 Hz), 19.9 (s)
5	2035s, 1957s, 1902s[g]	7.32 (m, 20H)	2.81 (m, 4H), 1.61[i]				

[a] ν(CO) in C_6H_6 unless noted. [b] In $CDCl_3$ for **1a**, **1b**, and **5**; in DMSO-d_6 for **2a–d**, **3a**; and in C_6D_6 for **4**. [c] In DMSO-d_6 for **2a**, **2c**, **2d**, and **3b** and in C_6D_6 for **4**. [d] Resonances due to terminal CO unless otherwise noted and the lowest field resonances correspond to two COs trans to the corresponding phosphorous atoms of the P–P ligands. [e] Phenyl resonances are observed as multiplets at δ 138.0–127.8. The dimer acid **3b** also shows a triplet at δ 128.0 due to solvated C_6D_6. [f] Resonances due to methylene carbons unless otherwise noted. [g] In CH_2Cl_2. [h] In nujol mulls. [i] (qn 5 Hz).

Reaction of Re(CO)$_3$(P–P)CO$_2$H with MeOH and EtOH: ester (alkoxycarbonyl) formation

Treatment of the hydroxycarbonyls with a THF solution of diazomethane left them unchanged, attesting to the very low acidity of these complexes. On the other hand, the esters are readily prepared when the hydroxycarbonyls are dissolved in

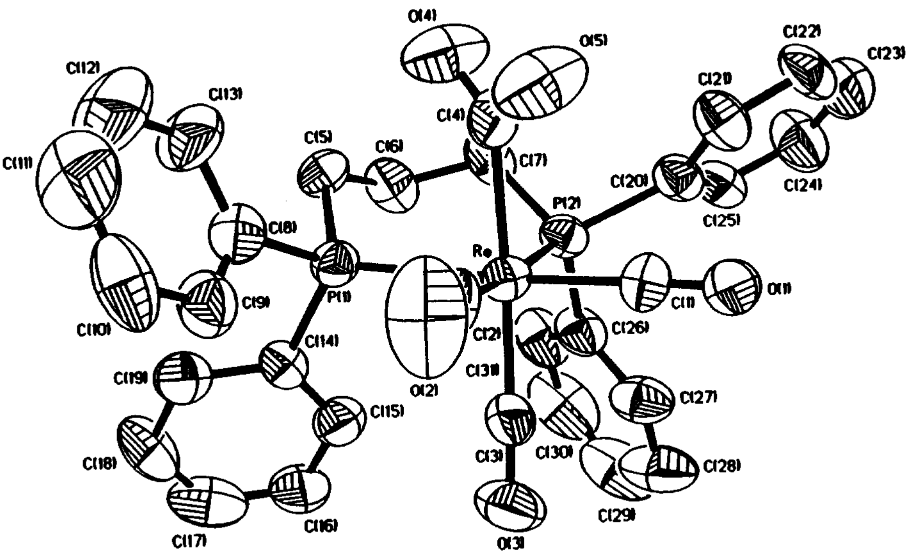

Fig. 1. Perspective drawing of molecule **3b**, *fac*-$Re(CO)_3(dppp)C(O)OD \cdot 0.5C_6D_6$.

alcohols (methanol and ethanol). However, the BF_4 salts **1a**, **1b** do not produce the esters when dissolved in alcohols. The addition of alkoxide to this stable solution of the salts leads to immediate ester formation. It is thus clear that undissociated alcohols are not sufficiently nucleophilic to react with the cation and that the conjugate base of the alcohol is required. In the esterification of the metallocarboxylic acids with alcohols in the absence of base, the conjugate base of the alcohol is generated from the reaction of the hydroxide anion, produced by ionization of the metallocarboxylic acid, with undissociated alcohol; the sequence of reactions is

$$Re(CO)_3(P\text{-}P)C(O)OH \rightleftharpoons [Re(CO)_4(P\text{-}P)]^+ + OH^-$$
$$HO^- + ROH \rightleftharpoons RO^- + H_2O$$
$$[Re(CO)_4(P\text{-}P)]^+ + OR^- \rightleftharpoons Re(CO)_3(P\text{-}P)C(O)OR$$

The reversibility of the last step can be demonstrated by the ease of achieving transesterification. Thus, for example, when the pure methyl ester is dissolved in ethanol and the solution is evaporated to dryness, pure ethyl ester is obtained. A similar initial dissociation of a metallocarboxylic acid has been suggested in the esterification of a $PtCO_2H$ complex [11].

X-ray structure of fac-*$Re(CO)_3(dppp)C(O)OD \cdot 0.5C_6D_6$ (3b)*

A view of the hydroxycarbonyl complex, *fac*-$Re(CO)_3(dppp)C(O)OD$ is presented in Fig. 1. Crystal data were obtained under the conditions summarized in Table 3.

The atomic coordinates and equivalent isotropic displacement parameters are given in Table 4 and selected bond lengths and angles are compiled in Table 5. The coordination geometry of the rhenium atom is roughly octahedral. The equatorial plane of the octahedron is occupied by two terminally bound carbonyl ligands and the phosphorus atoms of a chelating dppp ligand. One of the axial sites is also filled by a third terminally bound carbonyl ligand. A carboxyl group has

Table 3

Crystallographic data for *fac*-Re(CO)$_3$(dppp)C(O)OD·0.5C_6D_6 (**3b**) [a]

$C_{34}H_{26}D_4O_5P_2Re$	F.W. = 770.80
Crystal system orthorhombic	Space group *Pbca* (no. 61)
$a = 16.208(2)$ Å	$T = 294$ K
$b = 20.028(2)$ Å	$d_{calc.} = 1.60$ g cm^{-3}
$c = 19.716(2)$ Å	Radiation (λ) = Mo-K_α (0.71073 Å)
$V = 6400(1)$ Å^3	$\mu = 39.85$ cm^{-1}
$Z = 8$	$R = 0.0691$
$F(000) = 3032$	$R_w = 0.0678$
No. of variables = 364	Goodness of fit = 1.26

[a] Details of measurement: monochromator; highly oriented graphite crystal, scan type, $2\theta - \theta$; scan speed, 2–8°/min; scan range, 0.8° on either side of $K_{\alpha 12}$; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F) + |g|F^2]^{-1}$ and $g = 0.000800$.

been built into the remaining axial position. The equatorial bond lengths show a bit of asymmetry in the ligand bindings. The Re–P(1) and Re–P(2) lengths are 2.472(3) and 2.454(3) Å, respectively, and these significant differences would appear to be consistent with the differing steric environments of the two phosphorus atoms. The Re–CO lengths trans to these phosphorus atoms are Re–C(1) = 1.93(1) Å and Re–C(2) = 1.94(1) Å, and are thus equivalent within the observed errors. The third Re–CO length is also 1.94(1) Å and the Re–C(O)OD length trans to it is 2.19(1) Å. The latter length is appreciably longer than the Re–C(OH) length of 2.13(2) Å observed in Re$_3$(CO)$_{14}$(μ^3,η^3-CO$_2$H) [13]. Presumably, electronic effects resulting from the coordination of two additional rhenium atoms to the carboxylic acid group in this compound leads to an enhancement in the π-acceptor ability of the metallated carbon atom, thereby imparting more double bond character to and a shortening of this Re–carbon bond. The Re–C(O)D length is in excellent agreement with the value of 2.19(3) Å observed for Re–C(O)R complexes [14].

Not unexpectedly, pairs of *fac*-Re(CO)$_3$(dppp)C(O)OD molecules exist as hydrogen-bonded dimers in the solid state (see Fig. 2). This hydrogen bonding between two carboxylic acid groups has been observed in *trans*-Pt(C_6H_5)(PEt$_3$)$_2$CO$_2$H [7b] as well as in many organic carboxylic acids [15]. The observed O ··· O separation of 2.72(2) Å is in good agreement with the value of 2.695(8) Å found in the *trans*-Pt(C_6H_5)(PEt$_3$)$_2$CO$_2$H dimer, but is larger than values commonly seen in dimeric organic acids (2.63–2.67 Å). The O=COD and (O)C–OD lengths are 1.23(2) and 1.33(2) Å, respectively, and compare well to the values of 1.24(1) and 1.33(1) Å reported for *trans*-Pt(C_6H_5)(PEt$_3$)$_2$CO$_2$H. The Re–C=O, Re–C–OH and O=C–OH angles at the carboxylic acid carbon are 130.2(9), 116.6(10) and 112.9(12)°, respectively. The relative acuteness of the O=C–OH angle may in part be the result of steric repulsions between the phenyl groups and other ligands as they are pulled into close proximity with each other by the hydrogen-bonding forces in the solid.

Experimental

All reactions were carried out under an atmosphere of argon. Solvents were purified by standard methods. IR spectra were recorded on a Perkin–Elmer 1600

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *fac*-$Re(CO)_3(dppp)C(O)OD \cdot 0.5C_6D_6$ (**3b**)

Atom	*x*	*y*	*z*	U_{eq} [a]
Re	1269(1)	3652(1)	6254(1)	42(1)
P(1)	1389(2)	4598(2)	7056(2)	45(1)
P(2)	86(2)	249(2)	6881(2)	44(1)
O(1)	1121(7)	2520(5)	5209(5)	74(4)
O(2)	2686(9)	4208(7)	5342(6)	126(6)
O(3)	2636(7)	2816(6)	6995(5)	88(5)
O(4)	41(8)	4754(6)	5815(5)	90(5)
O(5)	595(9)	4259(6)	4972(5)	118(6)
C(1)	1177(9)	2948(6)	5596(7)	55(5)
C(2)	2189(9)	4014(7)	5716(7)	61(5)
C(3)	2101(9)	3115(7)	6741(7)	58(5)
C(4)	512(10)	4305(6)	5641(6)	58(5)
C(5)	398(8)	4918(6)	7372(7)	52(5)
C(6)	−146(9)	4394(7)	7722(7)	63(5)
C(7)	−573(8)	3899(7)	7274(7)	61(5)
C(8)	1891(10)	5311(7)	6675(6)	58(5)
C(9)	2699(10)	5278(8)	6530(8)	72(6)
C(10)	3111(12)	5804(10)	6193(8)	95(8)
C(11)	2653(19)	6359(12)	6014(11)	132(12)
C(12)	1852(18)	6394(10)	6183(12)	132(12)
C(13)	1461(11)	5888(7)	6495(8)	85(7)
C(14)	1961(8)	4481(6)	7848(5)	43(4)
C(15)	1960(9)	3889(7)	8191(7)	57(5)
C(16)	2356(9)	3825(7)	8815(8)	69(5)
C(17)	2737(10)	4341(10)	9120(8)	81(7)
C(18)	2745(9)	4935(9)	8790(7)	77(6)
C(19)	2353(9)	5023(7)	8167(7)	62(5)
C(20)	−701(8)	2766(7)	6420(6)	50(4)
C(21)	−821(8)	2832(8)	5735(7)	61(5)
C(22)	−1432(9)	2496(8)	5392(8)	69(6)
C(23)	−1932(11)	2045(8)	5773(11)	93(8)
C(24)	−1835(11)	1999(8)	6454(8)	86(7)
C(25)	−1217(8)	2352(7)	6767(8)	60(5)
C(26)	322(9)	2667(7)	7570(6)	56(5)
C(27)	772(9)	2092(7)	7392(8)	66(6)
C(28)	958(10)	1621(10)	7869(10)	95(8)
C(29)	700(13)	1692(12)	8527(10)	106(10)
C(30)	267(12)	2249(12)	8695(9)	100(9)
C(31)	79(10)	2744(8)	8237(7)	72(6)
C(1S)	5306(20)	4202(10)	5188(16)	106(13)
C(2S)	5627	4792	5456	64(8)
C(3S)	5334	5408	5230	132(7)
C(4S)	4721	5434	4734	123(16)
C(5S)	4399	4844	4466	94(12)
C(6S)	4692	4229	4692	129(16)

[a] U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Series FT-IR instrument. NMR spectra were recorded on a Bruker AC 250 (250.133 MHz, ^1H; 62.896 MHz, ^{13}C) spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Micro analyses were performed by

Table 5

Selected bond lengths (Å) and angles (°) for *fac*-Re(CO)$_3$(dppp)C(O)OD·0.5C$_6$D$_6$ (**3b**)

Re–P(1)	2.472(3)	P(2)–C(20)	1.839(13)
Re–P(2)	2.454(3)	P(2)–C(26)	1.831(14)
Re–C(1)	1.927(13)	O(1)–C(1)	1.151(16)
Re–C(2)	1.936(14)	O(2)–C(2)	1.160(20)
Re–C(3)	1.945(14)	O(3)–C(3)	1.167(18)
Re–C(4)	2.187(14)	O(4)–C(4)	1.227(18)
P(1)–C(5)	1.838(13)	O(5)–C(4)	1.331(15)
P(1)–C(8)	1.805(14)	C(5)–C(6)	1.535(18)
P(1)–C(14)	1.831(11)	C(6)–C(7)	1.497(19)
P(2)–C(7)	1.854(14)	O(4)···O(5′) [a]	2.72(2)
P(1)–Re–P(2)	88.8(1)	C(5)–P(1)–C(14)	101.4(6)
P(1)–Re–C(1)	176.5(4)	C(8)–P(1)–C(14)	103.2(6)
P(2)–Re–C(1)	91.0(4)	Re–P(2)–C(7)	116.1(4)
P(1)–Re–C(2)	91.0(4)	Re–P(2)–C(20)	118.6(4)
P(2)–Re–C(2)	175.3(4)	C(7)–P(2)–C(20)	100.2(6)
C(1)–Re–C(2)	88.8(6)	Re–P(2)–C(26)	114.6(5)
P(1)–Re–C(3)	93.9(4)	C(7)–P(2)–C(26)	104.9(6)
P(2)–Re–C(3)	96.1(4)	C(20)–P(2)–C(26)	100.2(6)
C(1)–Re–C(3)	89.7(6)	Re–C(1)–O(1)	178.5(12)
C(2)–Re–C(3)	88.6(6)	Re–C(2)–O(2)	173.7(12)
P(1)–Re–C(4)	86.0(3)	Re–C(3)–O(3)	173.9(12)
P(2)–Re–C(4)	90.6(4)	Re–C(4)–O(4)	130.2(9)
C(1)–Re–C(4)	90.4(5)	Re–C(4)–O(5)	116.6(10)
C(2)–Re–C(4)	84.7(6)	O(4)–C(4)–O(5)	112.9(12)
C(3)–Re–C(4)	173.3(6)	P(1)–C(5)–C(6)	114.6(9)
Re–P(1)–C(8)	111.5(4)	C(5)–C(6)–C(7)	116.9(11)
C(5)–P(1)–C(8)	105.1(6)	P(2)–C(7)–C(6)	116.4(9)
Re–P(1)–C(14)	118.6(4)	Re–P(1)–C(5)	115.4(4)

[a] Symmetry code: ′ = ($-x$, $1-y$, $1-z$).

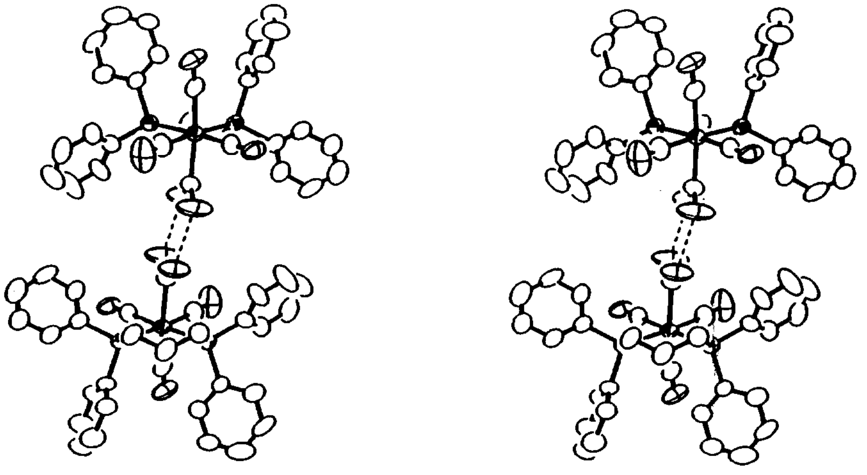

Fig. 2. A stereoview of the hydrogen bonding in **3b**, *fac*-Re(CO)$_3$(dppp)C(O)OD·0.5C$_6$D$_6$.

Galbraith Laboratories, Inc. $Re_2(CO)_{10}$, 1,2-bis(diphenylphosphino)ethane(dppe) and 1,3-bis(diphenylphosphino)propane(dppp) were purchased from commercial sources (either Pressure or Strem Chemical Co.). *fac*-$Re(CO)_3$(dppe)H [10a] and *fac*-$Re(CO)_3$(dppe)Br [16] were prepared by the referenced procedures.

Preparation of fac-*$Re(CO)_3$(dppe)H (4)*

A THF (75 ml) solution of $Re_2(CO)_{10}$ (2 g, 3.065 mmol) was placed in a flask containing sodium amalgam (0.4 g Na in 8 ml of Hg) and the mixture stirred for 2 h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ was transferred by cannula to another flask, the THF removed *in vacuo* and propanol (100 ml) and dppp (2.514 g, 6.095 mmol) were added to the solid residue. The solution was stirred for 10 h at room temperature, then refluxed for 6 h and cooled to 0°C. The precipitate which separated was dissolved in benzene (100 ml) and the solution passed over an alumina column. After concentrating the benzene solution, hexane was added and on cooling, the nearly white solid was filtered to give 2.45 g (3.583 mmol) of pure hydride.

Preparation of fac-*$Re(CO)_3$(dppp)Br (5)*

$Re(CO)_5Br$ [17] (1.0 g, 2.462 mmol) and dppp (1.015 g, 2.460 mmol) were mixed with 100 ml of benzene and refluxed for about 16 h. The solvent was removed using a rotary evaporator to yield a white solid residue (1.782 g, 2.337 mmol).

Preparation of $[ReCO)_4(P–P)]^+BF_4^-$ (1a, b)

To a solution of approximately 3 mmol of *fac*-$Re(CO)_3$(P–P)Br in 100 ml of refluxing CH_2Cl_2 was added a slight excess of $AgBF_4$ while a stream of CO was bubbled through the solution. After about 16 h, the solution was cooled and filtered through a pad of celite. The filtrate was concentrated and a small quantity of ether was added to precipitate the salt, $[Re(CO)_4(P–P)]^+BF_4^-$. Finally, vacuum drying afforded almost white **1a**, **b**.

Preparation of fac-*$Re(CO)_3$(P–P)C(O)OX (2a–d)*

To about 0.45 mmol of $[Re(CO)_4(P–P)]^+BF_4^-$ (**1a**, **b**) dissolved in about 7 ml of CH_3CN at 0°C was added an equivalent amount of 1 *M* NaOX (X = H, D) solution; the mixture was stirred briefly. The almost-white solid that formed was isolated by filtration, washed with hexane (2 × 5 ml) and vacuum dried to give **2a–d**. The ^1H NMR spectra of all these compounds showed the presence of solvated CH_3CN but before ultimate analysis, the samples of **2b** and **2c** were pumped free of solvent.

Preparation of $Re(CO)_3$(dppp)C(O)OX · $0.5C_6X_6$ (3a, b)

About 0.05 mmol of the acid (**2c**, **d**) was dissolved in 2 ml of C_6X_6 (X = H or D). The solution was kept at room temperature for about 16 h. The white diffraction grade quality crystals of the dimers **3a** and **3b** that formed were isolated by filtration, washed with benzene and vacuum dried.

Reaction of the hydroxycarbonyl complexes, fac-*$Re(CO)_3$(P–P)C(O)OX (2a–d) with ROH*

About 0.05 mmol of **2a–d** was dissolved in 50 ml of ROH (R = CH_3, C_2H_5). After 5 min the solvent was removed on a rotary evaporator and the alkoxycarbonyls, *fac*-Re(CO)$_3$(P–P)C(O)OR [18*] were obtained in almost quantitative yield. When pure methyl ester was dissolved in ethanol and the solution evaporated to dryness, pure ethyl ester was obtained and when pure ethyl ester was dissolved in methanol and the solution evaporated, pure methyl ester was obtained.

*Attempted reaction of **2a** and **2c** with diazomethane*

About 100 mg of either **2a** or **2c** were each treated separately with a large excess of CH_2N_2 in THF. The mixtures were stirred for 1 h and the solution then evaporated to dryness. The residue was pure starting material in both cases.

*Decarboxylation of **2a** and **2c** in DMSO*-d_6

About 0.05 mmol of **2a** or **2c** was dissolved in 0.400 ml of DMSO-d_6 and the reaction solutions monitored by ^{1}H NMR. After 24 h, the only product from **2a** was the corresponding hydride, Re(CO)$_3$(dppe)H. After about the same length of time, only about 75% of **2c** had been converted to the hydride, Re(CO)$_3$(dppp)H. On the other hand, when a drop of 4 *M* KOH solution was added to a small quantity of either **2a** or **2c** in DMSO, a transient yellow color was observed and on immediate dilution with water, white precipitates of the corresponding hydrides were obtained.

*Decarboxylation of **2a** and **2c** in DMF*

A solution of 50 mg of **2a** or **2c** in 25 ml of DMF was left standing at room temperature and the IR spectra of the solutions were recorded periodically. After about 2 days, only a trace of the corresponding hydrides, Re(CO)$_3$(P–P)H, were present; the major product was the bridging carbanato dimer, [Re(CO)$_3$(P–P)]$_2$(μ-O$_3$C). As with DMSO solutions, the addition of KOH to the DMF led to immediate decarboxylation of **2a** and **2c** to their corresponding hydrides.

*Thermal decarboxylation of **2a** and **2c***

When heated to their melting points (about 160°C), the hydroxycarbonyls **2a** and **2c** lose CO_2 and are converted quantitatively to their corresponding hydrides. The decarboxylation occurs more slowly at lower temperatures without melting.

*Ionization of **2a–d** in CH_2Cl_2*

About 0.05 mmol of **2a–d** was dissolved in 50 ml of CH_2Cl_2 and left standing at room temperature. The IR spectra, recorded periodically, showed that all of these compounds slowly but only slightly ionized to [Re(CO)$_4$(P–P)] (X = H or D).

*X-ray crystal structure of Re(CO)$_3$(dppp)C(O)OD · 0.5C$_6$D$_6$ (**3b**)*

Examination and data collection, using a colorless prism of **3b** (0.18 × 0.22 × 0.22 mm^3) sealed in a glass capillary were performed on a Siemens R3m/V four-circle diffractometer. Data were collected for $4.0° \leq 2\theta \leq 55.0°$ ($0 \leq h \leq +21$, $0 \leq k \leq +26$, $0 \leq l \leq +25$). Lorentz polarization corrections were applied to 8092 reflections. A semi-empirical absorption correction was applied ($T_{max} = 0.3307$, $T_{min} = 0.2715$). A total of 4187 reflections with $F \geq 3\sigma(F)$ were used in further calculations. The structure was solved by heavy-atom methods. The SHELXTL-PLUS programs [19] were used for data reduction, structure solution and refinement. The structure was refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were idealized with C–H = 0.96 Å and were assigned fixed isotropic temperature parameters U(H) = 0.08 Å^2. The benzene solvent molecule in the lattice was refined as a rigid regular hexagon with fixed carbon populations of 0.5 and with individual isotropic temperatures free to vary. The hydrogen atoms of the benzene molecule and the carboxylic acid group were not visible in any of the difference-Fourier maps and were not included in the refinements. The two largest residuals on the final difference map corresponded to 1.2 and 1.0 e$^-$/Å^3, and were 0.8 and 1.0 Å from the rhenium atom, respectively.

Details of structure factors and anisotropic temperature parameters are available from the authors.

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