# Reaction between $[Re_3H_3(CO)_{12}]$ and the Diphosphine Ligands $Ph_2PCH_2PPh_2$ and $(EtO)_2POP(OEt)_2$: *X*-Ray Crystal Structures of $[Re_2H_2(CO)_6(Ph_2PCH_2PPh_2)]$ † and $[Re_3H_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2]$ ‡

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The reactions of $[Re_3H_3(CO)_{12}]$ with the diphosphine ligands $Ph_2PCH_2PPh_2$ (dppm), $(EtO)_2POP(OEt)_2$ (tedip), and $Ph_2PCH_2CH_2PPh_2$ (dppe) have been studied. From the reaction with dppm, the known complex $[Re_2(CO)_8(dppm)]$ (1) has been isolated together with the three new complexes $[Re_2H_2(CO)_6(dppm)]$ (2), $[Re_3H_3(CO)_{10}(dppm)]$ (3), and $[Re_3H_3(CO)_8(dppm)_2]$ (4). The reaction of $[Re_3H_3(CO)_{12}]$ with tedip proceeds similarly to that with dppm, forming products (5), (6), and (7) analogous to (2), (3), and (4), and a second isomer of (6), $[Re_3H_3(CO)_{10}(tedip)]$ (8), in which a tedip ligand chelates a single rhenium atom in an axial–equatorial configuration. Protonation of (7) gives the cation $[Re_3H_4(CO)_8(tedip)_2]^+$ (10). Complexes (2) and (7) have been characterised by *X*-ray structure analysis by conventional heavy-atom methods using room-temperature diffractometer data. Complex (2) crystallises in space group *Pbca* with $Z = 8$, $a = 19.220(5)$, $b = 29.820(9)$, and $c = 10.655(4)$ Å, and (7) in space group $P2_1/c$ with $Z = 4$, $a = 18.053(6)$, $b = 16.211(5)$, $c = 14.800(3)$ Å, and $\beta = 102.41(2)$. Final residuals were $R = 0.033$ and 0.0696 for 2 247 and 3 398 unique observed intensity data respectively. In (2) the dppm ligand and two hydride ligands bridge the (formal) Re–Re double bond. In (7) the $Re_3(\mu\text{-}H)_3$ core of $[Re_3H_3(CO)_{12}]$ is preserved with four axial sites occupied by the two tedip ligands which bridge two edges of the $Re_3$ triangle. The reaction between $[Re_3H_3(CO)_{12}]$ and dppe gives $[ReH(CO)_3(dppe)]$ as the major product; a minor product isolated in low yield is formulated as $[Re_2H(CO)_7(Ph_2PCH_2CH_2PPhC_6H_4)]$ (9).

THE preparation of polynuclear transition-metal carbonyl complexes containing multidentate ligands which bridge or cap the metal atoms is of interest in that such bridging or capping ligands may confer stability on the cluster unit and prevent it breaking up into monomeric units on further reaction. Thus Masters and co-workers[1] have shown that the capped complex $[Ru_3(CO)_9\{(Bu^n{}_2P)_3SiMe\}]$ is more resistant to break up under high CO–$H_2$ pressures than the parent $[Ru_3(CO)_{12}]$. Similarly, we have reported that the bridged complex $[Re_2H_2(CO)_6(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$), the synthesis of which is described in this paper, tends to react as a dimer whereas the parent compound $[Re_2H_2(CO)_8]$ gives only mononuclear products even under mild reaction conditions.[2]

The reaction of bidentate phosphorus or arsenic donor ligands with the binary metal carbonyl complexes $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ has been well studied,[3-7] and has led to the synthesis of some bridged complexes, such as $[Mn_2(CO)_5(dppm)_2]$ with interesting properties.[8] The reaction of corresponding bidentate ligands with the trinuclear carbonyl hydride complexes $[M_3H_3(CO)_{12}]$ (M = Mn or Re) has not been reported, however, and in this paper the results of such an investigation for $[Re_3H_3(CO)_{12}]$ using the ligands $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2PPh_2$ (dppm), and $(EtO)_2POP(OEt)_2$ (tedip) are presented.

## RESULTS AND DISCUSSION

(a) *Reaction of* $[Re_3H_3(CO)_{12}]$ *with dppm.*—The reaction of $[Re_3H_3(CO)_{12}]$ with a 2 : 1 excess of dppm gave, after 40 min in refluxing octane, an orange-brown solution which contained none of the starting complex Four complexes were separated by thin-layer chromatography (t.l.c.) and identified spectroscopically (see below) as $[Re_2(CO)_8(dppm)]$ (1) (*ca.* 5%), $[Re_2H_2(CO)_6(dppm)]$ (2) (25%), $[Re_3H_3(CO)_{10}(dppm)]$ (3) (12%), and $[Re_3H_3(CO)_8(dppm)_2]$ (4) (30%) (approximate yields in parentheses). Proposed structures for these complexes are shown in Figure 1 and in the case of $[Re_2H_2(CO)_6(dppm)]$ this proposal has been confirmed by an *X*-ray diffraction study.

The mass spectrum of (1) shows a molecular-ion peak at *m/e* 982 (based on $^{187}Re$) and its identity was confirmed by comparison of its i.r. (Table 1) and $^1H$ n.m.r. spectra (Table 2) with those reported for this complex by Colton,[9] who has synthesised it from the reaction of $[Re_2(CO)_{10}]$ with dppm.

The mass spectrum of (2) shows the expected molecular-ion peak at *m/e* 928 ($^{187}Re$) and the proposed formulation is supported by microanalytical data. The $^1H$ n.m.r. spectrum shows, in addition to phenyl resonances, a triplet of relative intensity two at δ 3.13 p.p.m. ($J_{PH} = 10.8$ Hz), which can be assigned to the methylene protons of the ligand, and a further triplet of relative intensity two at δ −7.51 p.p.m. ($J_{PH} = 10.4$ Hz) due to the bridging metal hydride ligands. An electron count, assuming the proposed structure shown in Figure 1, reveals that the complex is two electrons short of that required by the effective atomic number (e.a.n.) rule unless a metal–metal double bond between the rhenium atoms is assumed. In order to investigate this possibility and confirm the proposed structure, an *X*-ray crystal-structure determination was undertaken.

The structure of (2) is shown in Figure 2; all H atoms have been omitted. The molecules exist as discrete

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† μ-Bis(diphenylphosphino)methane-di-μ-hydrido-bis-(tricarbonylrhenium)(2*Re–Re*).

‡ 1,1,1,2,2,2,3,3-Octacarbonyl-1,2:2,3:1,3-tri-μ-hydrido-1,3:2,3-bis-μ-tetraethyl diphosphite-*PP′*-*triangulo*-trirhenium.

TABLE 1

Infrared and microanalytical data for rhenium–diphosphine complexes

| | Compound | Solvent | $\tilde{\nu}$(CO)/cm$^{-1}$ | Analysis (%) [a] C | Analysis (%) [a] H |
|---|---|---|---|---|---|
| (1) | $[Re_2(CO)_8(dppm)]$ | Hexane | 2 072m, 2 019m, 1 981s, 1 955w, 1 942w, 1 921s | | |
| (2) | $[Re_2H_2(CO)_6(dppm)]$ | $CH_2Cl_2$ | 2 041s, 2 012s, 1 947m, 1 918s, br | 39.9(40.1) | 2.9(2.6) |
| (3) | $[Re_3H_3(CO)_{10}(dppm)]$ [b] | Hexane | 2 097m, 2 041s, 2 026s, 2 010m, 1 977s, 1 966s, 1 956vw, 1 946vw, 1 936m, 1 931m | 33.6(33.6) | 2.4(2.0) |
| (4) | $[Re_3H_3(CO)_8(dppm)_2]$ | $CH_2Cl_2$ | 2 027s, 2 011s, 1 947s, 1 921s, br, 1 871m | 45.5(44.8) | 3.8(3.0) |
| (5) | $[Re_2H_2(CO)_6(tedip)]$ | $CH_2Cl_2$ | 2 058s, 2 027s, 1 968m, 1 947m (sh), 1 933s | | |
| (6) | $[Re_3H_3(CO)_{10}(tedip)]$ (isomer 1) | Hexane | 2 102w, 2 054s, 2 036s, 2 009s, 1 994m, (sh), 1 992m, 1 970s, 1 945s | 19.7(19.6) | 2.2(2.1) |
| (7) | $[Re_3H_3(CO)_8(tedip)_2]$ | Hexane | 2 047w, 2 032s, 2 015w, 1 980m, 1 958m, 1 932m, 1 905w | 22.0(22.1) | 3.5(3.4) |
| (8) | $[Re_3H_3(CO)_{10}(tedip)]$ (isomer 2) | Hexane | 2 067w, 2 058w, 2 039m (sh), 2 031s, 2 013w, 1 980s, 1 959s, br, 1 932s, br, 1 899w (sh) | | |
| (9) | '$[Re_2(CO)_7(dppe)]$' | Hexane | 2 080w, 2 028s, 1 983s, 1 974m, 1 950m, 1 938m, 1 932m | 40.7(41.0) | 2.6(2.5) |
| (10) | $[Re_3H_4(CO)_8(tedip)_2]^+$ | $CH_2Cl_2$ | 2 043m, 2 023s, 1 983s, 1 955s, 1 900m, v br | | |

[a] Calculated values are given in parentheses. [b] Analytical data for $[Re_3H_3(CO)_{10}(dppm)]\cdot 0.5CH_2Cl_2$.

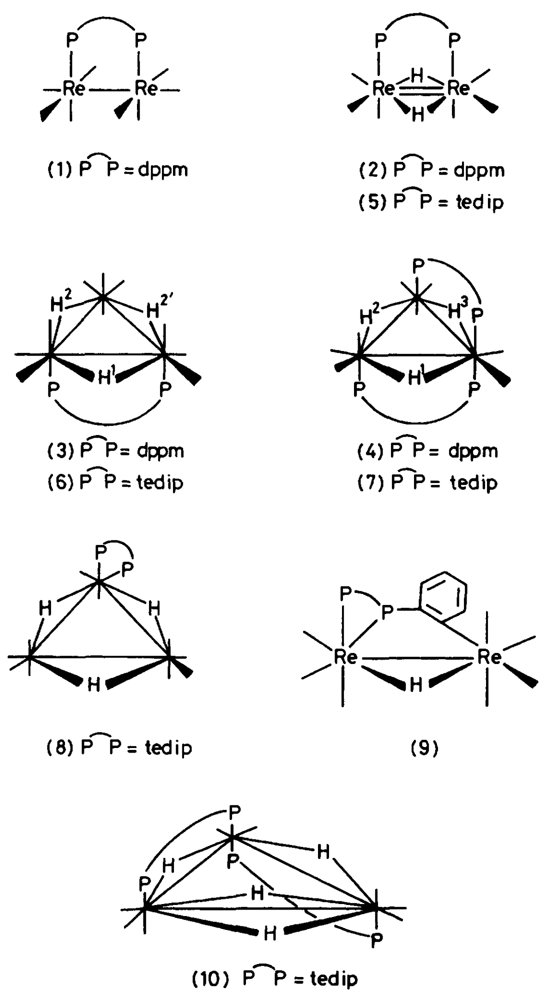

FIGURE 1 Proposed structures for some rhenium diphosphine complexes

TABLE 2

Proton and $^{13}C$ data (δ/p.p.m.) * for rhenium–diphosphine complexes

| Compound | |
|---|---|
| (a) $^1H$ n.m.r. | |
| (1) | 7.36 (m, 20 H, Ph), 4.39 (t, $J_{PH}$ = 10.0, 2 H, $CH_2$) |
| (2) | 7.24 (m, 20 H, Ph), 3.13 (t, $J_{PH}$ = 10.8, 2 H, $CH_2$), −7.51 (t, $J_{PH}$ = 10.4, 2 H, ReH) |
| (3) | 7.47 (m, 10 H, Ph), 7.20 (m, 10 H, Ph), 3.99, 2.67 (m, $J_{HH'}$ = 14.7, 2 H, $CH_2$), −15.51 (t, $J_{PH} + J_{PH'}$ = 24.2, 1 H, ReH), −16.41 (t, $J_{PH} + J_{P'H}$ = 14.4, 2 H, ReH) |
| (4) | 7.20 (m, 40 H, Ph), 5.09, 3.42 (m, $J_{HH'}$ = 15, 4 H, $CH_2$), −12.05 (m, 2 H, ReH), −13.16 (t, $J_{PH+P'H}$ = 16.6, 1 H, ReH) |
| (5) | 4.08 (m, $J_{HH'}$ = 6.9, 8 H, $CH_2$), 1.36 (t, $J_{HH'}$ = 6.9, 12 H, $CH_3$), −8.93 (t, $J_{PH}$ = 12.9, 2 H, ReH) |
| (6) | 4.02 (m, 8 H, $CH_2$), 1.33 (t, $J_{HH'}$ = 7.0, 12 H, $CH_3$), −16.43 (t, $J_{PH'}$ = 12.7, 1 H, ReH), −17.12 (t, $J_{PH} + J_{P'H}$ = 16.4 Hz, 2 H, ReH) |
| (7) | 4.02 (m, 16 H, $CH_2$), 1.31 (t, $J_{HH'}$ = 7, 24 H, $CH_3$), −16.66 (m, 2 H, ReH), −17.42 (t, $J_{PH+P'H}$ = 21.2, 1 H, ReH) |
| (8) | 4.03 (m, 8 H, $CH_2$), 1.32 (m, 12 H, $CH_3$), −16.57 (m, 1 H, ReH), −17.00 (m, 1 H, ReH), −17.26 (m, 1 H, ReH) |
| (9) | 7.43 (m, 19 H, Ph), 2.57 (m, 2 H, $CH_2$), −14.17 (d of d, $J_{PH}$ = 19.6, $J_{PH}$ = 13.4, 1 H, ReH) |
| (10) | 3.99 (m, 16 H, $CH_2$), 1.28 (m, 24 H, $CH_3$), −10.00 (m, 2 H, ReH), −12.80 (m, 2 H, ReH) |
| (b) $^{13}CO$ n.m.r. | |
| (2) | 194.1 (t, $J_{PC} + J_{P'C}$ = 74, 2CO), 193.4 (s, br, 4CO) |
| (3) | 190.3, 189.9, 188.7, 188.0, 187.5, 187.1, 185.8, 181.3, 180.9 |
| (c) $^{13}C$ Phenyl carbon atoms | |
| dppm | $C^1$ 140.0 (t, $J_{PC} + J_{P'C}$ = 7.8), $C^2$ 138.8 (t, $J_{PC} + J_{P'C}$ = 20.8), $C^3$ 129.5 (t, $J_{PC+P'C}$ = 7), $C^4$ 129.8 (s) |
| (3) | $C^2$ 133.9 (t, $J_{PC} + J_{P'C}$ = 11.4), $C^{2'}$ 133.1 (t, $J_{PC} + J_{P'C}$ = 11.0), $C^3$ 130.1 (t, $J_{PC} + J_{P'C}$ = 10.0), $C^{3'}$ 129.8 (t, $J_{PC+P'C}$ = 10.0), $C^4$ 132.2 (s), $C^{4'}$ 131.8 (s) |

* Recorded in $CD_2Cl_2$ solution at 35 °C: $^1H$ n.m.r. at 100 MHz, $^{13}C$ n.m.r. at 25.2 MHz; s = singlet, d = doublet, t = triplet, m = multiplet. Relative intensities are approximate only; *J* values in Hz.

neutral units separated by normal van der Waals distances. The final bond lengths and angles are presented in Tables 3 and 4 respectively. The two Re atoms and the two P atoms of the bridging dppm ligand are coplanar. The six carbonyl groups are terminal and, although the hydrides were not located directly, the distribution of the carbonyls indicates that the hydrides bridge the Re–Re bond and lie on either side of the $Re_2P_2$ plane. Four of the carbonyls bend away from the metal–metal bond with an average *cis* Re–Re–C (carbonyl) angle of 134.6(10)° compared to the expected angle of 90° for octahedrally co-ordinated Re in the absence of bridging hydrides; this assignment is in agreement with one based on potential-energy calculations.[10] The two P atoms exhibit distorted tetrahedral co-ordination geometry with the smallest C–P–C angle between the two phenyl rings. The two phenyl rings C(111)—C(116) and C(211)—C(216) are approximately parallel with an interplanar distance of 3.4 Å, which is indicative of graphitic packing.

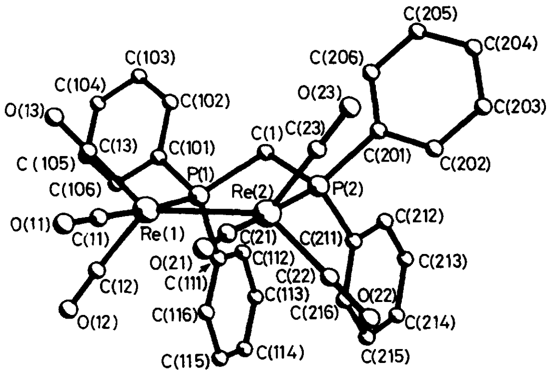

FIGURE 2 The molecular structure of $[Re_2H_2(CO)_6(dppm)]$ (2)

The observed rhenium–rhenium bond length at 2.893(2) Å is considerably shorter than that found in systems containing Re–Re single bonds, *e.g.* $[Re_2(CO)_{10}]$ (Re–Re 3.02 Å), or those with hydride ligands bridging Re–Re single bonds as in $[Re_3H_2(CO)_{12}]^-$ [Re(μ-H)Re 3.177 Å] [11] and (7) [Re(μ-H)Re 3.308 Å]. It is, however, similar to Re–Re bond lengths in other complexes where Re–Re double bonds have been postulated, *e.g.* $[Re_3H_3(CO)_{10}]$ (Re–Re 2.797 Å) [2–13] and $[Re_2H_2(CO)_8]$ (Re–Re 2.896 Å).[14] Complex (2) may, of course, be considered as a derivative of $[Re_2H_2(CO)_8]$ with two of the axial carbonyl groups in the parent complex being replaced by the diphosphine. Another rhenium complex which is closely related to (2) is $[Re_2(CO)_6(dpam)Cl_5]$ [15] (dpam = $Ph_2AsCH_2AsPh_2$) but in this complex the bridging Cl ligands each act as a three-electron donor, thereby enabling the complex to satisfy the e.a.n. rule without the need for a metal–metal bond, which is reflected in the much longer Re–Re distance of 3.81 Å.

TABLE 3

Bond lengths (Å) in (2) with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Re(2)–Re(1) | 2.893(2) | C(11)–Re(1) | 1.902(17) |
| P(1)–Re(1) | 2.449(4) | C(12)–Re(1) | 1.884(17) |
| P(2)–Re(2) | 2.457(4) | C(13)–Re(1) | 1.907(16) |
| C(1)–P(1) | 1.841(13) | C(21)–Re(2) | 1.845(18) |
| C(101)–P(1) | 1.813(11) | C(22)–Re(2) | 1.881(16) |
| C(111)–P(1) | 1.819(10) | C(23)–Re(2) | 1.879(16) |
| C(1)–P(2) | 1.851(13) | O(11)–C(11) | 1.184(18) |
| C(201)–P(2) | 1.824(9) | O(12)–C(12) | 1.176(17) |
| C(211)–P(2) | 1.816(9) | O(13)–C(13) | 1.159(16) |
| O(21)–C(21) | 1.222(19) | O(22)–C(22) | 1.180(17) |
| O(23)–C(23) | 1.188(16) | | |

The crystal structure of (2) shows, as found in other binuclear complexes where the metal atoms are bridged by dppm,[16] that the carbon atom of the methylene group is displaced from the plane of the two phosphorus and two metal atoms. This plane is then no longer a plane of mirror symmetry for the molecule as a whole and the lack of such symmetry renders both the two methylene hydrogen atoms and the two bridging hydride ligands non-equivalent. In solution, however, a triplet is observed in the $^1H$ n.m.r. for each of these two sets of hydrogen atoms, even at −96 °C, indicating that the $CH_2$ group is fluxional and that the activation-energy barrier for movement of this group from side to side of the plane containing the metal and phosphorus atoms is low. The $^{13}C$ n.m.r. spectrum of the complex shows that, apart from the methylene group ‘ flip,’ the molecule is non-fluxional over the temperature range −90 to +100 °C. Thus, the four carbonyl groups *cis* to the phosphine ligand give rise to a broad singlet at 193.4 p.p.m. while the *trans* carbonyls appear as a triplet centred at 194.1 p.p.m. ($J_{PC} + J_{P'C} = 74$ Hz).

TABLE 4

Bond angles (°) in (2) with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| P(1)–Re(1)–Re(2) | 90.0(1) | P(2)–Re(2)–Re(1) | 92.5(1) |
| C(11)–Re(1)–Re(2) | 90.8(5) | C(21)–Re(2)–Re(1) | 89.8(5) |
| C(11)–Re(1)–P(1) | 177.3(5) | C(21)–Re(2)–P(2) | 177.0(5) |
| C(12)–Re(1)–Re(2) | 132.3(5) | C(22)–Re(2)–Re(1) | 135.6(5) |
| C(12)–Re(1)–P(1) | 92.5(5) | C(22)–Re(2)–P(2) | 91.4(5) |
| C(12)–Re(1)–C(11) | 88.8(7) | C(22)–Re(2)–C(21) | 88.2(7) |
| C(13)–Re(1)–Re(2) | 138.2(5) | C(23)–Re(2)–Re(1) | 132.1(5) |
| C(13)–Re(1)–P(1) | 88.1(5) | C(23)–Re(2)–P(2) | 89.4(5) |
| C(13)–Re(1)–C(11) | 89.6(7) | C(23)–Re(2)–C(21) | 87.6(7) |
| C(13)–Re(1)–C(12) | 89.5(6) | C(23)–Re(2)–C(22) | 92.1(7) |
| C(1)–P(1)–Re(1) | 111.3(4) | C(1)–P(2)–Re(2) | 111.7(4) |
| C(101)–P(1)–Re(1) | 114.6(4) | C(201)–P(2)–Re(2) | 112.9(4) |
| C(101)–P(1)–C(1) | 102.9(5) | C(201)–P(2)–C(1) | 104.2(5) |
| C(111)–P(1)–Re(1) | 117.4(3) | C(211)–P(2)–Re(2) | 121.4(3) |
| C(111)–P(1)–C(1) | 107.2(5) | C(211)–P(2)–C(1) | 103.2(5) |
| C(111)–P(1)–C(101) | 102.1(5) | C(211)–P(2)–C(201) | 101.6(4) |
| P(2)–C(1)–P(1) | 109.4(7) | C(202)–C(201)–P(2) | 117.2(3) |
| C(102)–C(101)–P(1) | 121.4(3) | C(206)–C(201)–P(2) | 122.7(3) |
| C(106)–C(101)–P(1) | 118.5(3) | C(212)–C(211)–P(2) | 118.1(2) |
| C(112)–C(111)–P(1) | 120.4(3) | C(216)–C(211)–P(2) | 121.6(2) |
| C(116)–C(111)–P(1) | 119.5(3) | O(21)–C(21)–Re(2) | 174.7(15) |
| O(11)–C(11)–Re(1) | 176.5(15) | O(22)–C(22)–Re(2) | 176.8(14) |
| O(12)–C(12)–Re(1) | 176.9(14) | O(23)–C(23)–Re(2) | 179.6(11) |
| O(13)–C(13)–Re(1) | 179.7(8) | | |

Complex (3) does not give rise to a molecular-ion peak in its mass spectrum and at accelerating voltages of both 20 and 70 eV * the highest mass peaks observed are at $m/e$ = 1 198 $(M - CO)^+$ and 1 149 $(M - Ph)^+$. The complex has, however, been fully characterised as $[Re_3H_3(CO)_{10}(dppm)]$ by a combination of i.r. and n.m.r. ($^1H$, $^{13}C$ ligand, and $^{13}C$ carbonyl) spectroscopy and by microanalysis. Thus the i.r. spectrum shows eight ν(CO) bands indicating a molecule of low symmetry and in the $^1H$ n.m.r. there are two hydride resonances at δ −15.51 and −16.41 p.p.m. with respective relative intensities of 1 : 2. The methylene hydrogen atoms are

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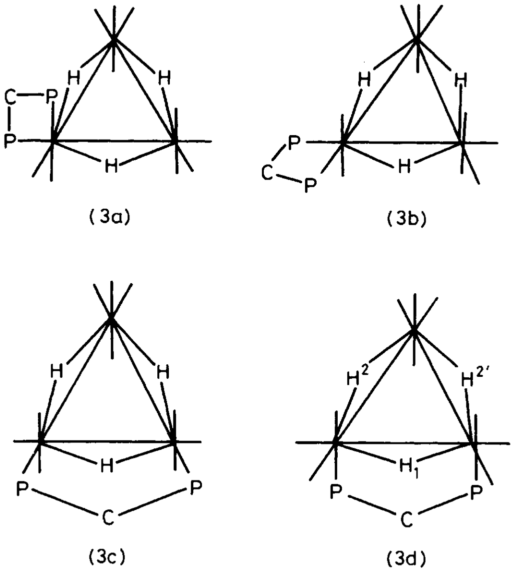
* Throughout this paper: 1 eV ≈ $1.60 \times 10^{-19}$ J.

inequivalent as indicated by the AB system obtained on $^{31}P$ decoupling and there are two distinct $^{1}H$ phenyl multiplet resonances at δ 7.5 and 7.2 p.p.m. of equal relative intensity. Bearing in mind the steric constraints imposed by the dppm ligand there are four possible structures for complex (3) which are depicted in Figure 3. Of these possibilities (3a) can be discounted as it has three inequivalent hydride ligands. Structure (3b) can also be discounted since, although the hydride resonances would occur in the intensity ratio 2 : 1, there is a mirror plane through the molecule in the plane of the $Re_3$ triangle which would cause the methylene hydrogen atoms and the phenyl groups to become equivalent. Structure (3c) could explain the observed spectra if the hydride ligand bridging the same edge of the rhenium triangle as the dppm ligand were to be displaced out of the plane defined by the metal atoms. Such a structure seems unlikely, however, on steric grounds as compared to structure (3d) which is entirely consistent with the observed $^{1}H$ spectrum.



(3a) (3b) (3c) (3d)

FIGURE 3 Possible structures for complex (3)

Complex (3d) gives two different environments for the methylene and phenyl protons since one half of the ligand projects over the metal triangle while the other half projects away from it. Clearly there are two hydride environments and the $^{1}H$ n.m.r. triplet resonance at δ −15.51 p.p.m. of relative intensity one may be assigned to $H^1$ coupled to the two phosphorus atoms. Atoms $H^2$ and $H^{2'}$ are chemically equivalent but magnetically nonequivalent, as are the two phosphorus atoms, so these form an AA'XX' system which results in the hydride resonance at δ −16.4 p.p.m. due to $H^2H^{2'}$ also appearing as a triplet. No coupling between the two types of hydride ligands was detected.

The above structural assignment for (3) is further confirmed by the $^{13}C$ n.m.r. of the ligand phenyl carbon atoms. In the $^{1}H$-decoupled $^{13}C$ spectrum of the free ligand $C^1$ (δ 140.0), $C^2$ (δ 133.8), and $C^3$ (δ 129.5) appear as triplets and $C^4$ (δ 129.8) as a singlet. In the spectrum of (3) (again $^{1}H$ decoupled) $C^1$ and $C^{1'}$ were not detected but the other features of the spectrum are consistent with the presence of two equally populated environments for the phenyl groups. Thus $C^2$ and $C^{2'}$ occur at δ 133.9 and 133.1, $C^3$ and $C^{3'}$ at δ 130.1 and 129.8 p.p.m. The resonances arising from $C^4$ and $C^{4'}$ are shifted appreciably downfield on complexing, to δ 132.2 and 131.8 p.p.m. respectively.

The $^{13}C$ carbonyl n.m.r. spectrum was recorded using a sample prepared from $[Re_3H_3(CO)_{13}]$ enriched to approximately 20% in $^{13}CO$. Unfortunately the spectrum, although relatively sharp, could not be reliably assigned due to overlapping signals. It was, however, invariant over the temperature range −80 to +100 °C indicating the stereochemical rigidity of the complex, although it seems likely that the methylene group ' flips ' as in (2). Neither this flipping nor the scrambling of hydride ligands would necessarily be apparent from the $^{13}C$ n.m.r. spectrum, but hydride scrambling is ruled out by the $^{1}H$ n.m.r. spectrum in which the resonances due to these ligands are also invariant over the same temperature range.

The substitution of dppm on the bis axial position in (3) may be contrasted with the substitution in the bis equatorial position which is observed for the related molecules $[Ru_3(CO)_{10}(dppm)]$ [17] and $[Os_3(CO)_{10}(dppm)]$.[18] The greater tendency for axial substitution in $[Re_3H_3(CO)_{12}]$ as compared to $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ is apparent, however, from previous studies on phosphine substitution in these molecules; [19-21] it may be correlated [21] with the large intermetal separations in the rhenium complex and the steric influence of the μ-H ligands.

Complex (4) was identified as $[Re_3H_3(CO)_8(dppm)_2]$ by microanalysis and from spectroscopic data. A mass spectrum could not be recorded for this complex since its volatility was too low even at a source temperature of 200 °C. Its structure (Figure 1) has been assigned by analogy with that of $[Re_3H_3(CO)_8(tedip)_2]$ (7) for which *X*-ray (see below) and neutron-diffraction [22] studies provide confirmatory evidence. In accord with the proposed structure for (4), its $^{1}H$ n.m.r. shows that two types of hydride ligand (δ −12.05 and −13.16 p.p.m., intensity ratio 2 : 1) are present and that there are two environments for the methylene hydrogen atoms (δ 5.09 and 3.42 p.p.m., $J_{HH}$ = 15 Hz). Complexes (4) and (7) represent the first reported examples of tetrasubstituted derivatives of $[Re_3H_3(CO)_{12}]$.

(b) *Reaction of* $[Re_3H_3(CO)_{12}]$ *with tedip*.—This reaction proceeds in an analogous fashion to that between $[Re_3H_3(CO)_{12}]$ and dppm apart from the fact that no $[Re_2(CO)_8(tedip)]$ was isolated. The complexes $[Re_2H_2(CO)_6(tedip)]$ (5), $[Re_3H_3(CO)_{10}(tedip)]$ (6), and $[Re_3H_3(CO)_8(tedip)_2]$ (7) were formed in similar yields to their dppm analogues. All the complexes gave a molecular-ion peak in their mass spectra and were further characterised by microanalyses and comparison of i.r. and $^{1}H$

n.m.r. data with those for their dppm analogues. One further trinuclear complex was obtained in low yield in the reaction with tedip which does not have a dppm analogue. Its mass spectrum shows a molecular-ion peak corresponding to the formulation $[Re_3H_3(CO)_{10}(tedip)]$, (8), and (8) is therefore an isomer of (6). The i.r. spectrum of (8) is completely different from that of (6), however, and contains many more peaks, indicating a molecule of lower symmetry. The $^1H$ n.m.r. spectrum shows three equally intense peaks in the hydride region (δ −16.57, −17.00, and −17.26 p.p.m.) and the most reasonable structure in accord with this spectrum (Figure 1) places the tedip ligand chelating a single rhenium atom in an axial–equatorial fashion. The spectrum is also consistent with the tedip ligand bridging two rhenium atoms in an axial–equatorial fashion but the ' bite ' of the tedip ligand seems unlikely to allow this. The molecular structure of (7) is shown in Figure 4; all H atoms have been omitted. The crystal structure consists of isolated neutral $[Re_3H_3(CO)_8(tedip)_2]$ molecules separated by normal van der Waals distances. The final bond lengths and angles are given in Tables 5 and 6. As predicted on spectroscopic grounds, the molecular geometry shows (non-crystallographic) $C_2$ symmetry with four axial sites in the ligand polyhedron occupied by the two tedip ligands. The metal co-ordination is therefore similar to that observed for the manganese congener, $[Mn_3H_3(CO)_{12}]$,[23] of the parent carbonyl $[Re_3H_3(CO)_{12}]$, the principal differences arising since two edges of the $Re_3$ triangle are bridged by the tedip ligands. In contrast, in $[Re_3H_3(CO)_{11}(PPh_3)]$,[24] the substituent ligand is in an equatorial position, this being the predominant (71%) species in solution. As discussed above, the bis axial co-ordination geometry is favoured for both dppm and tedip probably on steric grounds; transoid bis axial co-ordination of two pyridine ligands to the $[Re_3H_3(CO)_{10}]$ unit has been observed.[24] The Re–Re distances [mean 3.383(17) Å] are in good agreement with other hydride-bridged Re–Re lengths in related trinuclear complexes: *cf.* $[Re_3H_3(CO)_{11}(PPh_3)]$ 3.262(12),[25] $[Re_3H_3(CO)_{10}(C_5H_5N)_2]$ 3.292,[24] $[Re_3H_2(CO)_{12}]^-$ 3.18 Å,[11] and substantially longer than the Re–Re single-bond distance in *e.g.* $[Re_2(CO)_{10}]$ 3.02 Å.[12] The tedip bridged Re–Re distances are noticeably contracted relative to the Re(2)–Re(3) edge which is bridged by hydride alone [3.261(5) *vs.* 3.308 (2) Å]. This is presumably a consequence of the bite of the ligand being smaller than the 'natural' Re(μ-H)Re distance; this bite is best measured by the P(1) ··· P(3) and P(2) ··· P(4) distances [mean 2.915(10) Å]. This disparity in ligand bite *vs.* metal–metal separation is reflected in the geometry of the Re–P–O–P–Re linkages which show some twisting away from planarity, and is most marked for the central oxygens which lie, on average, 0.15 Å from their $Re_2P_2$ planes. A less extended geometry for the P–O–P moiety within a similar ligand $[OP(OMe)OP(OMe)_2]$ has been observed in an $Os_5$ cluster complex,[26] where the Os–Os bond bridged was appreciably shorter, corresponding distances [(7) first] being: metal–metal 3.261(5), 2.836(2); P ··· P 2.915(10), 2.81(1); P–O (bridge) 1.62(2), 1.64(1) Å; P–O–P 128.7(8), 118(1)°.

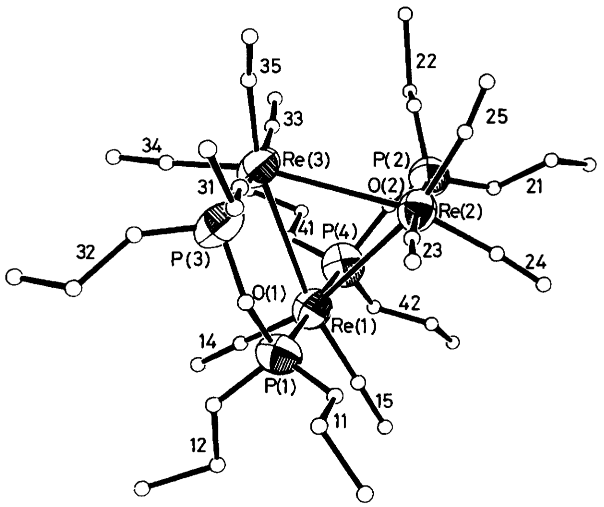


FIGURE 4 The molecular structure of $[Re_3H_3(CO)_8(tedip)_2]$ (7)

TABLE 5

Bond lengths (Å) for $[Re_3H_3(CO)_8(tedip)_2]$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Re(2)–Re(3) | 3.308(2) | | |
| Re(1)–Re(2) | 3.253(2) | Re(1)–Re(3) | 3.269(2) |
| Re(1)–P(1) | 2.348(7) | Re(1)–P(4) | 2.347(7) |
| Re(2)–P(2) | 2.367(7) | Re(3)–P(3) | 2.365(7) |
| Re(1)–C(14) | 1.91(4) | Re(1)–C(15) | 1.86(3) |
| Re(2)–C(23) | 1.92(3) | Re(2)–C(24) | 1.85(3) |
| Re(2)–C(25) | 1.93(3) | Re(3)–C(33) | 1.91(3) |
| Re(3)–C(34) | 1.96(4) | Re(3)–C(35) | 2.00(4) |
| P(1)–O(1) | 1.62(2) | P(3)–O(1) | 1.58(2) |
| P(2)–O(2) | 1.59(2) | P(4)–O(2) | 1.67(2) |
| P(1)–O(11) | 1.56(2) | P(1)–O(12) | 1.62(2) |
| P(2)–O(21) | 1.60(2) | P(2)–O(22) | 1.61(2) |
| P(3)–O(31) | 1.64(3) | P(3)–O(32) | 1.62(3) |
| P(4)–O(41) | 1.61(2) | P(4)–O(42) | 1.61(3) |
| O(11)–C(111) | 1.54(3) | C(111)–C(112) | 1.54(4) |
| O(12)–C(121) | 1.35(4) | C(121)–C(122) | 1.58(6) |
| O(21)–C(211) | 1.48(5) | C(211)–C(212) | 1.59(5) |
| O(22)–C(221) | 1.47(4) | C(221)–C(222) | 1.72(6) |
| O(31)–C(311) | 1.46(6) | C(311)–C(312) | 1.32(7) |
| O(32)–C(321) | 1.54(7) | C(311)–C(322) | 1.22(8) |
| O(41)–C(411) | 1.49(4) | C(411)–C(412) | 1.36(6) |
| O(42)–C(421) | 1.37(6) | C(421)–C(422) | 1.41(7) |
| C(14)–O(14) | 1.18(4) | C(15)–O(15) | 1.15(3) |
| C(23)–O(23) | 1.18(3) | C(24)–O(24) | 1.16(3) |
| C(25)–O(25) | 1.10(4) | C(33)–O(33) | 1.22(3) |
| C(34)–O(34) | 1.15(4) | C(35)–O(35) | 1.07(4) |

The hydride ligands were not located in this study but bridge the three edges of the $Re_3$ triangle; the H atoms lie close to the plane of this triangle, occupying *cis* octahedral sites on each rhenium atom. This assignment of position has been confirmed by a combined *X*-ray–neutron structure analysis, details of which will be reported elsewhere, and by a potential-energy technique.[10] Comparison of the M–M–CO(*cis*-equatorial) angles in this complex with those in $[Os_3(CO)_{12}]$, a complex with a similar non-hydride ligand arrangement (*i.e.* twinned cubo-octahedral), shows the steric effect of the hydride ligands in the equatorial plane {mean angles 104.0(5)° in (7) and 98.2(4)° in $[Os_3(CO)_{12}]$}. The remaining features of the ligand geometries are unremarkable with averaged parameters as follows: bond lengths Re–P(*trans* to CO) 2.366(7), Re–P(*trans* to P) 2.347(7), Re–C 1.91(2), (Re)C–O 1.15(3), P–O(ethoxy) 1.61(2), O–$CH_2$ 1.47(3), C–C 1.47(3) Å; bond angles Re–C–O 174.2(2.0), P–O–C 125(3)°.

TABLE 6

Interbond angles (°) for $[Re_3H_3(CO)_8(tedip)_2]$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Re(2)–Re(1)–Re(3) | 60.9(1) | Re(2)–Re(1)–P(1) | 90.8(2) |
| Re(2)–Re(1)–C(14) | 164.3(1.0) | Re(2)–Re(1)–C(15) | 104.5(1.0) |
| Re(2)–Re(1)–P(4) | 87.2(2) | Re(3)–Re(1)–P(1) | 86.7(2) |
| Re(3)–Re(1)–P(4) | 91.5(2) | Re(3)–Re(1)–C(14) | 103.8(1.0) |
| Re(3)–Re(1)–C(15) | 164.2(1.0) | P(1)–Re(1)–P(4) | 177.8(3) |
| P(1)–Re(1)–C(14) | 92.2(1.0) | P(1)–Re(1)–C(15) | 87.4(9) |
| P(4)–Re(1)–C(14) | 89.4(1.0) | P(4)–Re(1)–C(15) | 94.0(9) |
| C(14)–Re(1)–C(15) | 91.0(1.4) | Re(1)–Re(2)–Re(3) | 59.8(1) |
| Re(1)–Re(2)–P(2) | 85.0(2) | Re(1)–Re(2)–C(23) | 98.6(9) |
| Re(1)–Re(2)–C(24) | 105.3(1.0) | Re(1)–Re(2)–C(25) | 164.3(8) |
| Re(3)–Re(2)–P(2) | 88.0(2) | Re(3)–Re(2)–C(23) | 94.7(8) |
| Re(3)–Re(2)–C(24) | 165.0(1.0) | Re(3)–Re(2)–C(25) | 106.3(9) |
| P(2)–Re(2)–C(23) | 176.3(9) | P(2)–Re(2)–C(24) | 89.7(8) |
| P(2)–Re(2)–C(25) | 87.3(9) | C(23)–Re(2)–C(24) | 88.3(1.1) |
| C(23)–Re(2)–C(25) | 89.4(1.2) | C(24)–Re(2)–C(25) | 88.3(1.3) |
| Re(1)–Re(3)–Re(2) | 59.3(1) | Re(1)–Re(3)–P(3) | 84.2(2) |
| Re(1)–Re(3)–C(33) | 97.8(9) | Re(1)–Re(3)–C(34) | 106.7(1.1) |
| Re(1)–Re(3)–C(35) | 160.6(1.0) | Re(2)–Re(3)–P(3) | 93.1(2) |
| Re(2)–Re(3)–C(33) | 96.3(9) | Re(2)–Re(3)–C(34) | 165.7(1.1) |
| Re(2)–Re(3)–C(35) | 103.5(1.0) | P(3)–Re(3)–C(33) | 170.0(1.0) |
| P(3)–Re(3)–C(34) | 87.6(1.0) | P(3)–Re(3)–C(35) | 88.2(9) |
| C(33)–Re(3)–C(34) | 82.5(1.4) | C(33)–Re(3)–C(35) | 92.8(1.3) |
| C(34)–Re(3)–C(35) | 90.8(1.5) | Re(1)–P(1)–O(1) | 117.7(6) |
| Re(1)–P(1)–O(11) | 116.1(7) | Re(1)–P(1)–O(12) | 116.7(8) |
| O(1)–P(1)–O(11) | 103.9(1.0) | O(1)–P(1)–O(12) | 96.0(1.1) |
| O(11)–P(1)–O(12) | 103.6(1.0) | Re(2)–P(2)–O(2) | 121.0(8) |
| Re(2)–P(2)–O(21) | 116.9(8) | Re(2)–P(2)–O(22) | 114.9(8) |
| O(2)–P(2)–O(21) | 97.4(1.1) | O(2)–P(2)–O(22) | 99.1(1.1) |
| O(21)–P(2)–O(22) | 104.4(1.0) | Re(3)–P(3)–O(1) | 119.9(7) |
| Re(3)–P(3)–O(31) | 114.6(1.0) | Re(3)–P(3)–O(32) | 113.2(9) |
| O(1)–P(3)–O(31) | 99.7(1.1) | O(1)–P(3)–O(32) | 100.9(1.1) |
| O(31)–P(3)–O(32) | 106.6(1.3) | Re(1)–P(4)–O(2) | 117.8(8) |
| Re(1)–P(4)–O(41) | 114.4(9) | Re(1)–P(4)–O(42) | 118.8(9) |
| O(2)–P(4)–O(41) | 98.9(1.1) | O(2)–P(4)–O(42) | 102.6(1.2) |
| O(41)–P(4)–O(42) | 101.4(1.3) | P(1)–O(1)–P(3) | 129.3(1.1) |
| P(2)–O(2)–P(4) | 128.1(1.2) | P(1)–O(11)–C(111) | 118.9(1.6) |
| O(11)–C(111)–C(112) | 100.4(2.3) | P(1)–O(12)–C(121) | 123.4(2.5) |
| O(12)–C(121)–C(122) | 106.7(3.5) | P(2)–O(21)–C(211) | 122.8(2.4) |
| O(21)–C(211)–C(212) | 101.6(3.6) | P(2)–O(22)–C(221) | 115.5(2.3) |
| O(22)–C(221)–C(222) | 93.5(3.2) | P(3)–O(31)–C(311) | 135.4(3.1) |
| O(31)–C(311)–C(312) | 111.6(5.0) | P(3)–O(32)–C(321) | 143.0(3.0) |
| O(32)–C(321)–C(322) | 118.1(6.0) | P(4)–O(41)–C(411) | 120.8(2.3) |
| O(41)–C(411)–C(412) | 104.1(3.6) | P(4)–O(42)–C(421) | 120.0(3.5) |
| O(42)–C(421)–C(422) | 111.6(5.2) | Re(1)–C(14)–O(14) | 179.2(3.3) |
| Re(1)–C(15)–O(15) | 177.3(2.9) | Re(2)–C(23)–O(23) | 174.1(2.4) |
| Re(2)–C(24)–O(24) | 175.5(3.0) | Re(2)–C(25)–O(25) | 171.2(3.0) |
| Re(3)–C(33)–O(33) | 173.5(2.6) | Re(3)–C(34)–O(34) | 176.8(3.5) |
| Re(3)–C(35)–O(35) | 166.0(3.3) | | |

(c) *Reaction of* $[Re_3H_3(CO)_{12}]$ *with dppe*.—This reaction proceeds very differently from those with dppm and tedip. The major product, obtained in *ca*. 45% yield, is $[ReH(CO)_3(dppe)]$, identified as the facial isomer by comparison of spectroscopic data with those reported by Flitcroft and co-workers.[27,28] Several other low-yield products were obtained but only one of these, (8), could be separated by t.l.c., eluting as a light yellow band with the highest $R_f$ value after $[ReH(CO)_3(dppe)]$. Complex (9), obtained as colourless crystals, showed a peak with an *m/e* of 938 ($^{187}Re$) in its mass spectrum corresponding to the formulation $[Re_2(CO)_6(dppe)]$. Its solution i.r. spectrum exhibits seven peaks in the ν(CO) region indicating a molecule of low symmetry and that the peak at *m/e* 938 in its mass spectrum is, perhaps, $(M - CO)^+$. Certainly, microanalytical data would be consistent with the formulation of (9) as either $[Re_2(CO)_7(dppe)]$ or $[Re_2(CO)_6(dppe)]$, and the former possibility perhaps allows a more reasonable interpretation of its spectroscopic properties and most likely structure. Thus, the $^1H$ n.m.r. of (9) contains a signal in the bridging hydride region (δ −14.17 p.p.m.) which is split into a doublet of doublets by coupling to two inequivalent phosphorus atoms. This spectrum suggests that metallation of at least one phenyl ring has occurred and that (9) should, perhaps, be written as $[Re_2H(CO)_7(Ph_2PCH_2CH_2PPhC_6H_4)]$ with the structure shown in Figure 1. Unfortunately the crystals obtained for (9) proved not to be suitable for an *X*-ray analysis and did not allow this suggestion to be confirmed.

(d) *Protonation of Diphosphine-substituted Trimers*.—Attempts to protonate $[Re_3H_3(CO)_{12}]$ using concentrated $H_2SO_4$ or $CF_3COOH$ were unsuccessful, and no reaction occurred even after several days at room temperature. The disubstituted trinuclear complexes (3) and (6), each containing a single diphosphine ligand (dppm and tedip respectively), were also unreactive towards $CF_3COOH$ but the corresponding tetrasubstituted complexes (4) and (7) both dissolved in this acid to give brown solutions. The $^1H$ n.m.r. spectrum of (4) contained a broad unresolved hydride resonance at $\delta$ $-10.19$ p.p.m. and very broad resonances in the methyene and phenyl regions indicating that extensive decomposition had occurred. The $^1H$ n.m.r. of (7), however, contained two complex multiplets ($\delta$ $-10.00$ and $-12.80$ p.p.m.) which collapsed to two equal-intensity sharp singlets on $^{31}P$ decoupling. This change was reversible; on adding methanolic KOH the brown colour was completely discharged and unchanged (7) was precipitated from solution. Thus, it appears that (7) singly protonates in $CF_3COOH$ to give $[Re_3H_4(CO)_3(tedip)_2]^+$ (10) and the structure of (10) can be deduced from the n.m.r. spectra to be as depicted in Figure 1. Attempts to isolate (10) as a crystalline solid by precipitation with a large anion were unsuccessful.

The above protonation experiments indicate that substitution of carbonyl ligands by ligands which are better electron donors facilitates protonation of the metal-atom framework. This result is not unexpected and is in accord with previous studies on substituted trinuclear osmium complexes.[29]

## EXPERIMENTAL

All manipulations were carried out under dry oxygen-free nitrogen. Solvents were dried, deoxygenated, and distilled before use according to standard literature methods.

Infrared spectra were recorded in 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer using CO gas as calibrant. Mass spectra were obtained on an A.E.I. MS12 spectrometer using tris(perfluoroheptyl)-*s*-triazine as reference. Hydrogen-1 and carbon-13 n.m.r. spectra were recorded using a Varian Associates XL-100 spectrometer and calibrated relative to $SiMe_4$ using the solvent resonances as internal standards. Microanalyses were carried out at the Chemical Laboratory, University of Cambridge.

*Reactions of* $[Re_3H_3(CO)_{12}]$. (*a*) *With dppm.* The complex $[Re_3H_3(CO)_{12}]$ (0.20 g, 0.22 mol) and dppm (0.09 g, 0.45 mol) were refluxed in octane (20 $cm^3$), with stirring, for 40 min. During this time the solution gradually darkened from colourless to orange-brown. The solvent was removed under vacuum and the residue dissolved in the minimum quantity of $CH_2Cl_2$. The products were then separated by t.l.c. on silica using 30% acetone–70% hexane as eluant. The order of elution (decreasing $R_f$ values) was $[Re_2(CO)_8(dppm)]$ (1), $[Re_2H_2(CO)_6(dppm)]$ (2), $[Re_3H_3(CO)_{10}(dppm)]$ (3), and $[Re_3H_3(CO)_8(dppm)_2]$ (4), with approximate yields as given earlier. Final purification was achieved by recrystallisation from $CH_2Cl_2$–hexane, this being particularly important for (2) and (3) which have very similar $R_f$ values and could not be satisfactorily separated by t.l.c. alone.

(*b*) *With tedip.* The complex $[Re_3H_3(CO)_{12}]$ and tedip (0.12 g, 0.45 mol) were refluxed together in octane (20 $cm^3$) for 2 h during which time the solution gradually darkened in colour. The octane was removed on a rotary evaporator and the products were separated by t.l.c. on silica using 50% $CH_2Cl_2$–50% hexane as eluant. The order of elution (decreasing $R_f$ values, approximate percentage yields in parentheses) was $[Re_2H_2(CO)_6(tedip)]$ (5) (14%), $[Re_3H_3(CO)_{10}(tedip)]$ (6) (14%), $[Re_3H_3(CO)_8(tedip)_2]$ (7) (24%), and $[Re_3H_3(CO)_{10}(tedip)]$ (8) (6%). All were purified by recrystallisation from $CH_2Cl_2$–hexane.

(*c*) *With dppe.* The complex $[Re_3H_3(CO)_{12}]$ (0.20 g, 0.22 mol) and dppe (0.09 g, 0.45 mol) were refluxed in octane (20 $cm^3$) with stirring for 30 min. A highly insoluble yellow powder (which could not be characterised) precipitated out of solution during this time. The solution itself was then taken to dryness on the rotary evaporator and the residue dissolved in the minimum quantity of $CH_2Cl_2$. T.l.c. on silica using 30% acetone–70% hexane as eluant gave $[ReH(CO)_3(dppe)]$ as the major product (45%) and several other minor products in low variable yield. The light yellow band with the highest $R_f$ value gave $[Re_2(CO)_7(dppe)]$ (9), on crystallisation from $CH_2Cl_2$–hexane. An effective separation of the other minor products could not be achieved.

X-*Ray Structural Analysis of* $[Re_2H_2(CO)_6(dppm)]$ (2).—Orange-yellow rectangular blocks of (2) were obtained from a hexane–dichloromethane (1 : 1) solution by slow evaporation. Several suitable crystals were mounted on glass fibres. Preliminary cell dimensions were determined *via* Weissenberg (Cu-$K_\alpha$ radiation) photography.

A crystal with dimensions 0.23 × 0.08 × 0.09 mm, mounted about the crystallographic *c* axis, was transferred to an automated Stoe STADI-2 two-circle diffractometer. The *a* and *b* cell parameters were refined by a least-squares fit to the diffractometer zero-layer $\omega$ angle measurements. The axis length for *c* was determined accurately by using a second crystal mounted about *a*. 2 769 Intensities were recorded (layers 0–*hk*12) using Mo-$K_\alpha$ radiation and a 33-step scan procedure.

Lorentz polarisation and empirical absorption corrections (based on an azimuthal scan of the 006 reflection) were applied. Equivalent reflections were averaged to give 2 247 unique observed intensities [$F > 3\sigma(F)$].

*Crystal data.* $C_{31}H_{24}O_6P_2Re_2$, $M = 926.84$, Orthorhombic, $a = 19.220(5)$, $b = 29.820(9)$, $c = 10.655(4)$ Å, $U = 6\,106.8$ Å$^3$, $D_m$ not measured, $Z = 8$, $D_c = 2.02$ g cm$^{-3}$, $F(000) = 3\,503.22$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 81.40 cm$^{-1}$, space group *Pbca* from systematic absences.

The two Re atom positions were located by multisolution $\Sigma_2$ sign expansion, and all the remaining non-hydrogen atoms from subsequent electron-density difference synthesis. The C atoms of the phenyl rings were constrained to be regular hexagons with C–C distances of 1.395 Å. The H atoms were not located directly but the phenyl and methylene H atoms were constrained to lie in geometrically idealised positions, with C–H bonds fixed at 1.08 Å. The structure was refined by full-matrix least squares with the weighting scheme $w = 1.7639/[\sigma^2(F) + 0.0006(F_o)^2]$. The parameters refined included anisotropic thermal parameters for Re and P, and interlayer scale factors. The constraint $U_{33} = \frac{1}{2}(U_{11} + U_{22})$ was applied to reduce correlation involving interlayer scale factors. The refinement converged to $R = 0.033$ and $R' = 0.036$ [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}(F_o)$]. A final difference electron-density synthesis did not show any remaining regions of significant electron density.

X-*Ray Structural Analysis of* $[Re_3H_3(CO)_8(tedip)_2]$ (7).—Colourless tablets of (7) were grown from slowly evaporated hexane–dichloromethane solution. The space group and approximate cell dimensions were determined as for (2). A crystal of dimensions *ca.* 0.35 × 0.33 × 0.12 mm was mounted in a glass fibre in air for room-temperature data collection on a Syntex *P*2 diffractometer. Accurate cell dimensions were derived by least-squares fit to the diffractometer setting angles for 15 reflections in the range $20 < 2\theta < 26°$. 5 084 Reflection intensities were measured in a unique quadrant of reciprocal space, using the θ—2θ scan technique, in the range $2 < 2\theta < 60°$ with graphite-monochromated Mo-$K_\alpha$ radiation. Scan speeds varied between 1 and 29.3° min$^{-1}$; reflections with prescan counts below a low threshold were not remeasured. The measured intensities were corrected for crystal decay (*ca.* 8%), and absorption using a five-parameter fit to 384 azimuthal scan data; transmission coefficients for the full data set varied between 0.616 and 0.138. Lorentz and polarisation corrections were applied and equivalent data merged to yield unique data of which 3 398 with $F > 2\sigma(F)$ were used in the structure determination and refinement.

*Crystal data.* $C_{24}H_{43}O_{18}P_4Re_3$, $M$ = 1 487.8, Monoclinic, $a$ = 18.053(6), $b$ = 16.211(5), $c$ = 14.800(3) Å, $\beta$ = 102.41(2)°, $U$ = 4 230(2) Å$^3$, $D_m$ not measured, $Z$ = 4, $D_c$ = 2.04 g cm$^{-3}$, $F(000)$ = 2 463, $\lambda$ — 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 88.6 cm$^{-1}$, $T$ = 295 K, $2\theta_{max.}$ = 60°, space group $P2_1/c$ from systematic absences.

TABLE 7

Atomic co-ordinates (× $10^4$) for [$Re_2H_2(CO)_6$(dppm)] with estimated standard deviations in parentheses

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Re(1) | 1 976(1) | 1 138(1) | −1 894(1) |
| Re(2) | 1 094(1) | 1 019(1) | 282(1) |
| P(1) | 2 919(2) | 1 403(1) | −535(3) |
| P(2) | 1 950(2) | 1 368(1) | 1 687(3) |
| C(1) | 2 578(7) | 1 721(5) | 813(12) |
| C(101) | 3 507(5) | 1 799(3) | −1 271(9) |
| C(102) | 3 459(5) | 2 258(3) | −1 036(9) |
| C(103) | 3 902(5) | 2 556(3) | −1 655(9) |
| C(104) | 4 392(5) | 2 394(3) | −2 508(9) |
| C(105) | 4 440(5) | 1 935(3) | −2 742(9) |
| C(106) | 3 997(5) | 1 637(3) | −2 123(9) |
| C(111) | 3 517(5) | 985(2) | 83(9) |
| C(112) | 4 078(5) | 1 114(2) | 832(9) |
| C(113) | 4 541(5) | 792(2) | 1 281(9) |
| C(114) | 4 444(5) | 341(2) | 980(9) |
| C(115) | 3 883(5) | 212(2) | 231(9) |
| C(116) | 3 420(5) | 534(2) | −217(9) |
| C(201) | 1 555(5) | 1 753(2) | 2 811(9) |
| C(202) | 1 164(5) | 1 565(2) | 3 781(9) |
| C(203) | 821(5) | 1 842(2) | 4 635(9) |
| C(204) | 868(5) | 2 307(2) | 4 519(9) |
| C(205) | 1 259(5) | 2 495(2) | 3 549(9) |
| C(206) | 1 602(5) | 2 218(2) | 2 695(0) |
| C(211) | 2 506(5) | 1 033(2) | 2 698(9) |
| C(212) | 2 902(5) | 1 254(2) | 3 603(9) |
| C(213) | 3 386(5) | 1 016(2) | 4 315(9) |
| C(214) | 3 474(5) | 557(2) | 4 123(9) |
| C(215) | 3 077(5) | 336(2) | 3 218(9) |
| C(216) | 2 593(5) | 573(2) | 2 505(9) |
| C(11) | 1 239(9) | 961(5) | −2 976(16) |
| O(11) | 804(7) | 850(5) | −3 700(13) |
| C(12) | 2 570(9) | 743(6) | −2 764(14) |
| O(12) | 2 927(7) | 481(4) | −3 280(12) |
| C(13) | 2 216(8) | 1 604(5) | −3 043(14) |
| O(13) | 2 364(6) | 1 885(4) | −3 745(10) |
| C(21) | 415(9) | 771(6) | −727(16) |
| O(21) | −65(9) | 601(5) | −1 305(15) |
| C(22) | 929(8) | 555(6) | 1 440(14) |
| O(22) | 859(6) | 265(4) | 2 182(11) |
| C(23) | 396(8) | 1 380(5) | 993(14) |
| O(23 | −43(7) | 1 610(4) | 1 437(11) |

TABLE 8

Atomic positional parameters for [$Re_3H_3(CO)_8(tedip)_2$] with estimated standard deviations in parentheses

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Re(1) | 0.685 7(1) | 0.466 3(1) | 0.314 9(1) |
| Re(2) | 0.864 8(1) | 0.457 0(1) | 0.310 0(1) |
| Re(3) | 0.755 9(1) | 0.602 3(1) | 0.193 2(1) |
| P(1) | 0.711 4(5) | 0.561 9(4) | 0.436 7(4) |
| P(2) | 0.824 8(5) | 0.368 9(4) | 0.181 2(5) |
| P(3) | 0.764 3(6) | 0.686 6(4) | 0.325 5(4) |
| P(4) | 0.664 3(5) | 0.372 4(5) | 0.191 2(5) |
| O(1) | 0.752 7(10) | 0.647 6(10) | 0.419 4(10) |
| O(2) | 0.737 4(12) | 0.349 1(11) | 0.143 1(12) |
| C(14) | 0.580 0(24) | 0.490 8(22) | 0.289 1(22) |
| O(14) | 0.514 6(17) | 0.505 4(16) | 0.274 2(16) |
| C(15) | 0.673 4(19) | 0.387 6(19) | 0.401 6(19) |
| O(15) | 0.663 1(14) | 0.338 0(15) | 0.453 1(15) |
| C(23) | 0.903 9(18) | 0.525 9(17) | 0.415 1(19) |
| O(23) | 0.927 8(12) | 0.561 9(12) | 0.484 0(13) |
| C(24) | 0.902 1(18) | 0.366 6(18) | 0.381 9(18) |
| O(24) | 0.921 8(15) | 0.310 6(15) | 0.430 2(16) |
| C(25) | 0.961 2(19) | 0.464 6(18) | 0.274 2(19) |
| O(25) | 1.011 2(17) | 0.472 6(16) | 0.243 6(17) |
| C(33) | 0.733 6(20) | 0.545 2(18) | 0.077 4(21) |
| O(33) | 0.718 4(14) | 0.516 6(13) | −0.000 4(15) |
| C(34) | 0.671 3(24) | 0.671 6(24) | 0.131 9(24) |
| O(34) | 0.622 6(18) | 0.711 3(17) | 0.092 1(18) |
| C(35) | 0.829 8(23) | 0.677 7(22) | 0.152 2(21) |
| O(35) | 0.876 8(17) | 0.716 4(17) | 0.147 4(17) |
| O(11) | 0.759 5(11) | 0.529 7(10) | 0.530 2(11) |
| C(111) | 0.785 8(19) | 0.591 2(19) | 0.609 9(20) |
| C(112) | 0.787 2(26) | 0.534 5(25) | 0.694 0(26) |
| O(12) | 0.638 9(13) | 0.604 5(13) | 0.466 0(13) |
| C(121) | 0.591 9(28) | 0.563 8(26) | 0.509 9(26) |
| C(122) | 0.519 3(31) | 0.619 7(28) | 0.502 7(30) |
| O(21) | 0.854 2(12) | 0.275 9(12) | 0.192 0(12) |
| C(211) | 0.935 4(28) | 0.254 0(29) | 0.209 8(28) |
| C(212) | 0.931 8(28) | 0.160 9(29) | 0.176 5(28) |
| O(22) | 0.846 0(12) | 0.400 2(12) | 0.086 7(13) |
| C(221) | 0.809 3(28) | 0.355 2(27) | 0.002 7(28) |
| C(222) | 0.862 0(31) | 0.404 3(30) | −0.065 6(31) |
| O(31) | 0.847 1(15) | 0.730 6(15) | 0.361 9(16) |
| C(311) | 0.882 6(36) | 0.778 8(37) | 0.443 1(39) |
| C(312) | 0.919 1(29) | 0.843 6(31) | 0.420 1(30) |
| O(32) | 0.702 0(15) | 0.759 5(15) | 0.311 0(15) |
| C(321) | 0.649 8(41) | 0.808 6(40) | 0.360 6(41) |
| C(322) | 0.599 6(36) | 0.849 8(35) | 0.313 8(37) |
| O(41) | 0.605 7(13) | 0.404 1(13) | 0.100 6(14) |
| C(411) | 0.587 0(27) | 0.352 1(26) | 0.016 0(28) |
| C(412) | 0.542 8(30) | 0.401 7(30) | −0.048 0(31) |
| O(42) | 0.629 9(16) | 0.282 9(16) | 0.206 0(16) |
| C(421) | 0.675 1(35) | 0.223 9(39) | 0.257 1(36) |
| C(422) | 0.643 7(34) | 0.144 4(35) | 0.239 7(35) |

The Re atomic positions were located as for (2) by standard heavy-atom techniques. The rhenium and phosphorus atoms were assigned anisotopic, and all other non-hydrogen atoms isotropic, thermal parameters. Unconstrained refinement of all atomic parameters converged smoothly to final residuals $R$ = 0.0696, $R'$ = 0.0697 with weighting scheme $w = [\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$; hydridic and ethoxy-hydrogens were not located or incorporated in the refinement model. A final-difference electron-density synthesis showed no regions of significant electron density. The molecular geometry and labelling scheme is illustrated in Figure 4.

Complex neutral-atom scattering factors were employed throughout.[30] Final atomic co-ordinates for (2) and (7) are given in Tables 7 and 8 respectively, while details of thermal parameters, hydrogen-atom co-ordinates, and observed and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 23213 (38 pp.).* All computations were carried out on the University

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

of Cambridge IBM 370/165 computer using the SHELX 76 program system.[31] Figure 2 was drawn with the PLUTO program written by Dr. W. D. S. Motherwell. Figure 4 was drawn with ORTEP-II [32] written by Dr. C. K. Johnson.

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