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The reaction between unsaturated tetrarhenium cluster $H_4Re_4(CO)_{12}$ and tris(diphenylphosphino)methane

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Abstract

The reaction between the unsaturated cluster $H_4Re_4(CO)_{12}$ and tripod ($HC(PPh_2)_3$) was investigated. After refluxing the reactants in CH_2Cl_2 for 8 h, four compounds were isolated. They are identified by NMR, mass, IR and elemental analysis to be $HRe(CO)_3(\eta^2$-tripod), $H_2Re_2(CO)_6(\eta^3$-μ_2-tripod), $H_3Re_3(CO)_9(\eta^3$-μ_3-tripod) and $H_4Re_4(CO)_{12}(\eta^3$-μ_3-tripod). The structures of the trirhenium and tetrarhenium cluster products were determined by X-ray diffraction method. In $H_3Re_3(CO)_9$(tripod), the tripod ligand is capping on top of the Re_3 plane. The three rhenium atoms and the three phosphorus atoms form a slightly distorted trigonal prism. Though the Re–Re and Re–P bond distances show the presence of steric strain, $H_3Re_3(CO)_9$(tripod) is thermally much more stable than the uncapped $H_3Re_3(CO)_{12}$. In $H_4Re_4(CO)_{12}$(tripod), the four rhenium atoms form a spiked triangular configuration. Re4 is bonded to Re1 and is nearly perpendicular to the Re1–Re2–Re3 triangle. The three phosphorus atoms are coordinated to Re2, Re3 and Re4. A novel feature of this tetranuclear cluster is that one of the phenyl groups is coordinated in η^2-fashion through a double bond to Re4 which is in the spiked position. This is the first example of phenyl group coordination in tripod chemistry. The tetrarhenium cluster is also stable in refluxing CH_2Cl_2 in the presence of tripod.

Introduction

$H_4Re_4(CO)_{12}$, a 56-electron cluster, is an unusual "unsaturated" metal cluster. Both the IR and X-ray diffraction data [1] indicate that it is a highly symmetrical molecule. Resonance hybrids involving delocalized double bonds and face-centered μ_3-hydrides can satisfactorily account for the high symmetry feature of $H_4Re_4(CO)_{12}$:

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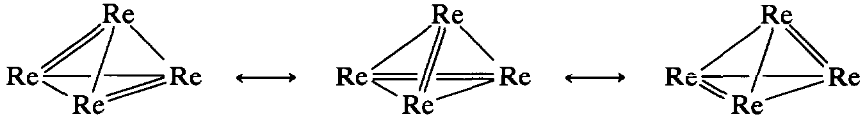


The Re–Re bond in $H_4Re_4(CO)_{12}$ is expected to be stronger than the Re–Re single bond because of the partial double bond character. In support to this expection, the bond length of 2.913 Å [1] is shorter than the hydride bridged Re–Re single bond (3.1–3.3 Å) or simple Re–Re single bond (3.02 Å) in $Re_2(CO)_{10}$ [2].

In spite of the strong Re–Re bond, $H_4Re_4(CO)_{12}$ is chemically reactive. It reacts rapidly with CO or PPh_3 [1], and leads to cluster degradation products. For CO reaction, $H_3Re_3(CO)_{12}$ and $HRe(CO)_5$ are produced. Besides CO and PPh_3, common solvents, such as acetone, acetonitrile and diethyl ether have been found to be reactive toward $H_4Re_4(CO)_{12}$ [1,3,4]. Other common solvents, such as alcohol, DMF, and THF, have also been found to be reactive to $H_4Re_4(CO)_{12}$ in our laboratory. To understand the chemistry of $H_4Re_4(CO)_{12}$, we sought to stabilize the tetrahedral framework by capping it with a tripod ligand $HC(PR_2)_3$ [5]. This tripod ligand exhibits several coordination modes. It can coordinate as η^3-μ_3 bridging ligand [6], η^3-μ_2 bridging ligand [7], η^2-μ_2 bridging ligand [8], or it can act as a simple tridentate [9], bidentate [7,10] or monodentate ligand [7b]. Furthermore, it can promote "spontaneous self assembly" of metal cluster such as $Ni_3(CO)_6(\mu_3\text{-}HC(PR_2)_3)$ from $Ni(CO)_4$ [11]. There are several known η^3-μ_3 tetranuclear clusters, such as $M_4(CO)_9$(tripod) (M = Co, Rh, Ir) [12] and $(\mu\text{-}H)_4Ru_4(CO)_9$(tripod) [13]. Indeed all these known capped tetrahedral clusters exhibit increased stability.

Unfortunately, when $H_4Re_4(CO)_{12}$ is reacted with $HC(PPh_2)_3$ in dichloromethane, the majority of the isolated products are products due to cluster degradation. Though a small amount of $H_4Re_4(CO)_{12}$(tripod) has been obtained, its structure, determined by X-ray diffraction, is a "spiked triangular" configuration similar to $H_4Re_4(CO)_{15}^{2-}$ [14] and $H_4Re_4(CO)_{15}I^-$ [15]. Also, a novel feature of this tetrarhenium cluster is that one of the phenyl group in the tripod ligand coordinates to Re in a η^2-fashion. The details of this reaction are reported herein.

Experimental section

General method

$Re_2(CO)_{10}$ and 1,1,1-tris(diphenylphosphino)methane $HC(P(C_6H_5)_2)_3$ were purchased from Strem Chemical Co. and were used without further purification. Solvents were purchased from Merck or Fluka Chemical Co. and were dried according to the standard methods [16].

^1H and ^{13}C NMR spectra were obtained on Bruker AM-400 or Varian Gemini-300 spectrometers. All chemical shifts were reported *vs.* TMS for both ^1H and ^{13}C spectra. ^{31}P NMR spectra were obtained on Bruker AM-400 or MSL-200 spectrometers. PPh_3 ($\delta = -6.00$ ppm) was used as an external standard. Mass spectra were recorded on a JEOL JMX-HX-110 mass spectrometer. IR spectra were obtained on a Bomen Michelson series 100 FTIR spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid instrument.

Table 1

^{1}H and ^{31}P NMR data [a] of rhenium–tripod complexes

Compound	^{1}H NMR	^{31}P NMR
$HRe(CO)_3$(tripod) (**1**)	-3.75 (t, 1H, J(PH) 47.7)	-3.66 (2P)
	5.62 (td, 1H, $J(P^2H)$ 11.74, $J(P^1H)$ 2.0)	19.48 (1P)
	6.88 ~ 7.71 (m, phenyl group)	
$H_2Re_2(CO)_6$(tripod) (**2**)	-14.4 (m, 2H)	4.63 (1P)
	5.87 (t, 1H, J(PH) 17.2)	-15.37 (1P)
	6.41 ~ 8.12 (m, phenyl group)	-15.83 (1P)
$H_3Re_3(CO)_9$(tripod) (**3**)	-15.30 (q, 3H, J(PH) 8.0)	14.50
	6.47 (q, 1H, J(PH) 9.4)	
	6.76 ~ 7.65 (m, phenyl group)	
$H_4Re_4(CO)_{12}$(tripod) (**4**)	-15.83 (d, 1H, J(PH) 9.9)	27.88 (1P)
	-15.34 (dd, 1H, J(PH) 15.1, J(P'H) 7.1)	35.80 (d, 1P)
	-14.36 (d, 1H, J(PH) 21.7)	40.06 (d, 1P)
	-13.73 (d, 1H, J(PH) 15)	J(PP) 100
	6.18 (m, 1H)	
	6.84 ~ 8.90 (m, phenyl group)	

[a] **1** and **2** were measured in $CDCl_3$, **3** and **4** were measured in CD_2Cl_2. Chemical shifts are in ppm from internal TMS (0 ppm) for ^{1}H NMR and external PPh_3 (-6.0 ppm) for ^{31}P NMR, and coupling constants are in Hz.

Preparation of $H_4Re_4(CO)_{12}$

$H_4Re_4(CO)_{12}$ was prepared according to the method of Kaesz [4] with some modification. $Re_2(CO)_{10}$ (0.72 g, 1.14 mmol) was dissolved in 350 ml decane. H_2 gas was bubbled through the solution under refluxing condition for 48 h. The solution slowly changed from colorless to deep red. Filter and keep the filtrate. The solid remaining in the reaction vessel and on the filter paper was dissolved with CH_2Cl_2. Filter and the filtrate is combined with the previous filtrate. Then, 30 ml benzene was slowly added to the solution. After 12 h, a deep red powder precipitated out. Recrystallization was carried out by dissolving the precipitate with 200 ml CH_2Cl_2 followed by adding 30 ml benzene. Collect the precipitate and dry it to give $H_4Re_4(CO)_{12}$ (0.51 g, 0.470 mmol). ^{1}H NMR (in $CDCl_3$): δ -5.04 ppm. IR (ν(CO), cm^{-1}): 2040s, 1980s, Mass (M^+, ^{187}Re): 1088.

Reaction of $H_4Re_4(CO)_{12}$ and tripod $HC(PPh_2)_3$

$H_4Re_4(CO)_{12}$ (0.12 g, 0.11 mmol) was added to CH_2Cl_2 solution (30 ml) containing $HC(PPh_2)_3$ (0.12 g, 0.22 mmol). The mixture was refluxed for 8 h under N_2. The color of the solution turned from deep red to pale yellow. And the reaction is completed. Four complexes were obtained after separation with silica gel PLC using toluene/hexane/$CHCl_3$ (1/1/1) as eluent. The PLC positions and yields of the four compounds are: $R_f = 0.44$, 48 mg for **1**; $R_f = 0.38$, 28 mg for **2**; $R_f = 0.31$, 80 mg for **3**; $R_f = 0.20$, 34 mg for **4**. All pertinent spectroscopic data of the four products are collected in Tables 1 and 2. Single crystals of **3** and **4** were obtained by slow evaporation of their respective $CHCl_3$ solutions.

X-ray crystallography

Single crystals of **3** and **4** were mounted in glass capillaries. Intensity data were collected in a Siemens R3m/V diffractometer using Mo-K_α radiation (0.7107 Å)

Table 2

Mass, IR and elemental analysis data for rhenium–tripod complexes

Compound	M^+, ^{187}Re	Analysis (Found (calc.) (%)) [a]		IR (ν(CO) cm^{-1}) [b]
		C	H	
HRe(CO)$_3$(tripod) (**1**)	840	53.85 (54.80)	4.04 (4.11)	1926.0br, 2006.2s 2034.4m
H$_2$Re$_2$(CO)$_6$(tripod) (**2**)	1112	45.89 (46.40)	3.07 (2.97)	1895.6m, 1955.3s, 2009.0s, 2034.9s
H$_3$Re$_3$(CO)$_9$(tripod) (**3**)	1384	35.86 (35.60)	2.30 (2.22)	1927.9s, 1952.6m, 1961.3m, 2017.6m, 2044.5s
H$_4$Re$_4$(CO)$_{12}$(tripod) (**4**)	1656	35.56 (35.60)	2.15 (2.11)	1899.6m, 1925.0s, 1945.3s, 1955.1m, 1966.9m, 1976.2m, 2007.0m, 2019.3s, 2037.7s, 2051.9s

[a] For **1**, it is calculated with extra two H_2O molecules. And for **3**, it is calculated with two molecules of $CHCl_3$. [b] All IR spectra were measured in chloroform solutions.

monochromatized from a highly oriented graphite crystal. Three standard reflections were measured every 50 reflections. The general data collection conditions and results are summarized in Table 3 for compounds **3** and **4**. The numbers of independent data are also reported in Table 3. The heavy atom positions were determined by the direct method. The non-hydrogen atoms were subsequently located from Fourier map and then anisotropically refined by full matrix least

Table 3

Summary of crystal data and intensity collection conditions for single crystals of **3** and **4**

	3	**4**
Formula	$Re_3C_{47}H_{39}O_{10}P_3Cl_3$	$Re_4C_{49}H_{35}O_{12}P_3$
Crystal size (mm)	0.32×0.12×0.10	0.34×0.34×0.41
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	12.632(4)	11.733(4), α 92.69(3)°
b (Å)	20.104(4), β 103.68°	12.390(6), β 92.89(3)°
c (Å)	22.459(10)	20.733(5), γ 114.92(3)°
V (Å^3)	5542(3)	2722(2)
Z	4	2
$d_{\text{calc.}}$ (g cm^{-3})	1.839	2.071
Abs. coeff. (cm^{-1})	69.09	91.32
Scan speed (deg min^{-1})	3.66–14.65	4.11–15.00
Ind. Refl.	7276	9621
Observed data with $I > 3\sigma$	2753	5954
R (%)	6.92	5.62
R_w (%)	7.12	6.62
Data parameter	7.6/1	9.7/1

squares. The positions of all hydrogen atoms were calculated and refined isotropically. R and R_w values after least-squares refinement are also reported in Table 3. All calculations were performed on a MicroVax II computer based on the Siemens SHELXTL PLUS program.

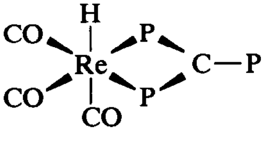
Results and discussion

$H_4Re_4(CO)_{12}$ was first synthesized by Kaesz's group in 1970 [1]. It was obtained by refluxing $H_3Re_3(CO)_{12}$ in decalin (b.p. 190°C) for 0.5 h under nitrogen. The yield was a meager 20%. A modified method of direct reaction between H_2 and $Re_2(CO)_{10}$ in decahydronaphthalene at 150–160°C for 24 h, produced $H_4Re_4(CO)_{12}$ with a yield of 43–51% [4]. Under our reaction conditions of elevated temperature (refluxing decane 174°C) and longer reaction time $\simeq 48$ h, the direct reaction between $Re_2(CO)_{10}$ and H_2 produces $H_4Re_4(CO)_{12}$ with a satisfactory yield of 82%, based on Re. This greatly facilitates the study of the chemistry of $H_4Re_4(CO)_{12}$.

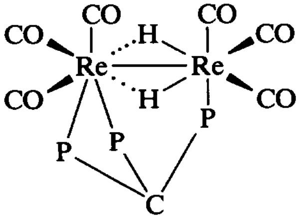
The reaction between $H_4Re_4(CO)_{12}$ and tripod ligand $HC(PPh_2)_3$ in refluxing CH_2Cl_2 is relatively slow. After refluxing for 8 h, four compounds were isolated by PLC. The spectroscopic data of these four compounds are listed in Tables 1 and 2. It has been observed that all ^{31}P NMR signals for the four compounds are broad. According to the mass and NMR data, all four compounds can be assigned straightforwardly. The reaction can be summarized by eq. 1.

$$\begin{aligned} H_4Re_4(CO)_{12} + HC(PPh_2)_3 \xrightarrow[\text{reflux}]{CH_2Cl_2} \; & \underset{(\mathbf{1},13\%)}{HRe(CO)_3(HC(PPh_2)_3)} \\ & + \underset{(\mathbf{2},11\%)}{H_2Re_2(CO)_6(HC(PPh_2)_3)} + \underset{(\mathbf{3},42\%)}{H_3Re_3(CO)_9(HC(PPh_2)_3)} \\ & + \underset{(\mathbf{4},19\%)}{H_4Re_4(CO)_{12}(HC(PPh_2)_3)} \qquad (1) \end{aligned}$$

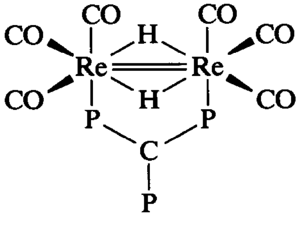
In **1**, the ^1H NMR data of hydride indicate clearly that two phosphorus atoms are coordinating to the metal. The ^{31}P NMR data also support this assignment. The two equivalent phosphorus atoms at -3.66 ppm are coordinated to Re, while the phosphorus atom at -19.48 ppm is not coordinated. There are several examples [7b,8,10] which indicate that the uncoordinated phosphorus atoms of tripod are at $\simeq -20$ ppm instead of the free tripod δ of -9.4 ppm. Hence its structure should be as depicted in I.



(I)



(II)



(II′)

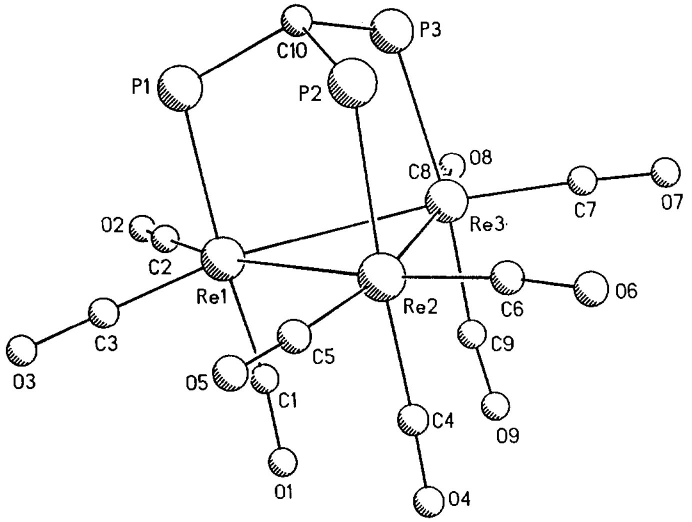


Fig. 1. ORTEP plot of $H_3Re_3(CO)_9$(tripod), showing the numbering scheme. All phenyl groups in the tripod ligand are omitted for clarity.

In **2**, the ^1H NMR signal of the hydrides is multiplet, indicating that the hydrides must couple to the coordinated phosphorus atoms nonequivalently. Both II and II′ are potential candidates for the structure of $H_2Re_2(CO)_6(HC(PPh_2)_3)$. The hydride pattern of AA′XYZ in II and AA′XX′ in II′ are expected to be multiplet. However, the ^{31}P NMR spectrum indicates that there is no uncoordinated PPh_2 group, which is expected to be around the free tripod ^{31}P chemical shift of −9.4 ppm, or the uncoordinated PPh_2 group in **1** (−19.48 ppm). Furthermore, the δ of hydride at −14.4 ppm is quite different from that reported for $H_2Re_2(CO)_8$ (−9.04 ppm) [17], $H_2Re_2(CO)_6$(dppm) (−7.51 ppm) [18] and $H_2Re_2(CO)_6$(tedip)(t, −8.93 ppm) [19]. Therefore, II is the more likely structure. Moreover, the number of CO vibrational bands is more than that expected for II′. For **3**, the hydride signal is typical of μ_2-edge-bridging hydride. And there is only one ^{31}P NMR signal. Hence, it is easy to deduce the structure to be a tripod capped triangular rhenium cluster. The tetrarhenium cluster **4** has four μ_2-bridged nonequivalent hydrides. Judging from its ^{31}P NMR data, all three phosphorus atoms in tripod are coordinated to Re. These points are verified by the X-ray structure analyses.

The molecular structure and numbering scheme of **3** is shown in Fig. 1. Selected bond distances and angles are listed in Table 4. The three rhenium atoms form a slightly distorted equilateral triangle. The mean Re–Re distance is 3.271 Å, which is longer than the normal Re–Re single bond length of 3.02 Å. It indicates unambiguously the presence of μ_2-bridging hydrides between each pair of rhenium atoms. The tripod ligand is capping on top of the Re triangular face. The Re2–Re1–P and the Re3–Re1–P angles are 84.7 and 90.8°, respectively. Similar configuration can be found around Re2 and Re3. Therefore, the triangular prism formed by the three rhenium atoms and the three phosphorus atoms in tripod ligand is slightly distorted, as depicted in Fig. 2. The average P–P distance is 3.11

Table 4

Selected bond distances (Å) and angles (deg) for $H_3Re_3(CO)_9$(tripod)

Re1–Re2	3.288(3)	Re1–Re3	3.273(3)
Re2–Re3	3.252(4)	Re1–P1	2.484(11)
Re2–P2	2.449(12)	Re3–P3	2.473(11)
P1–P2	3.093(16)	P2–P3	3.124(19)
P3–P1	3.110(17)	Re1–C1	1.830(68)
Re1–C2	1.934(60)	Re1–C3	1.846(52)
C1–O1	1.274(76)	C2–O2	1.107(72)
C3–O3	1.223(67)		
Re3–Re2–Re1	60.1(1)	Re2–Re1–Re3	59.4(1)
Re2–Re1–P1	84.7(3)	Re1–Re3–Re2	60.5(1)
Re3–Re2–P2	85.6(3)	Re3–Re1–P1	90.8(3)
Re1–Re3–P3	84.6(3)	Re1–Re2–P2	90.2(3)
C10–P1–Re1	110.4(14)	Re2–Re3–P3	90.8(3)
C10–P3–Re3	110.4(14)	C10–P2–Re(2)	111.2(13)
P2–C10–P3	109.8(20)	P1–C10–P2	109.7(23)
P1–Re1–C1	172.8(16)	P3–C10–P1	110.2(21)
C1–Re1–C2	91.6(25)	P1–Re1–C2	95.2(16)
C1–Re1–C3	89.3(25)	P1–Re1–C3	93.8(14)
Re1–C1–O1	173.3(39)	C2–Re1–C3	84.9(22)
Re1–C3–O3	179.3(39)	Re1–C2–O2	173.8(55)

Å which is only 0.16 Å shorter than the average Re–Re distances. This is shown clearly in Fig. 2, where the triangle of P1P2P3 is slightly smaller than the rhenium triangle.

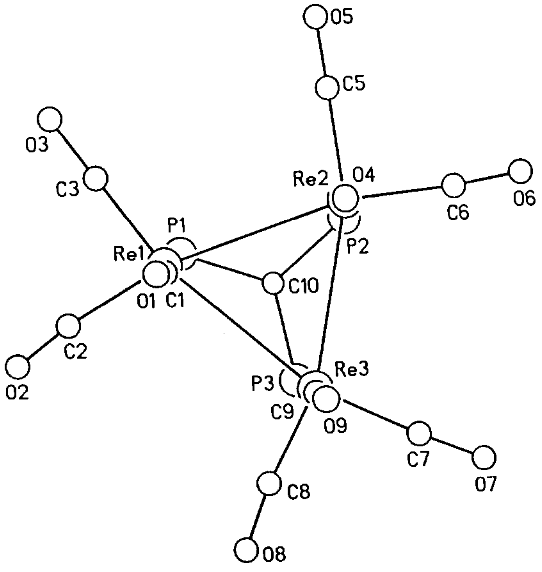


Fig. 2. ORTEP plot of $H_3Re_3(CO)_9$(tripod) projected into the plane formed by the three rhenium atoms. The phosphorus and rhenium trigonal prism is slightly twisted.

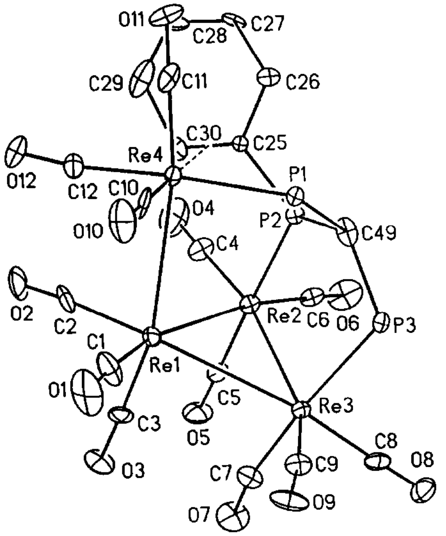


Fig. 3. ORTEP plot of $H_4Re_4(CO)_{12}$(tripod) showing the numbering scheme. All phenyl groups, except the one involved in π-bonding to Re4, are omitted for clarity.

It is noteworthy that the mean hydride bridged Re–Re distance in **3** is longer than that found in $H_3Re_3(CO)_{12}$ (3.241 Å) [20], $H_3Re_3(CO)_{11}(PPh_3)$(3.262 Å) [21], $H_2Re_3(CO)_{10}(PPh_3)_2^-$ (3.134 Å) [22], and $H_3Re_3(CO)_9(PPh_3)_3$ (3.259 Å) [23]. It is an indication that there is some strain in the tripod capped trirhenium cluster. This point is also supported by the data of Re–P distance. The average Re–P distance is 2.469 Å which is longer than that in $H_3Re_3(CO)_{11}(PPh_3)$ (2.421 Å), $H_2Re_3(CO)_{10}(PPh_3)_2^-$ (2.379 Å), and $H_3Re_3(CO)_9(PPh_3)_3$ (2.402 Å). It is also noteworthy that in $H_3Re_3(CO)_{11}(PPh_3)$, $H_2Re_3(CO)_{10}(PPh_3)_2^-$ and $H_3Re_3(CO)_9(PPh_3)_3$, all the triphenylphosphines are coordinated in radial positions. This is in direct contrast to **3** where all phosphorus atoms are coordinated in the axial positions.

The essential features of the structure of **4** and atomic numbering scheme are shown in Fig. 3. The four rhenium atoms form a spiked triangular configuration. Some selected bond distances and angles are collected in Table 5. The mean Re–Re distance in the Re1–Re2–Re3 equilateral triangle is 3.267 Å. The distance is only slightly smaller than that in **3**. Re4 bonds to Re1 and is almost perpendicular to the rhenium triangular plane. The Re4–Re1 distance is 3.435 Å which is much longer than the corresponding bond distances in the other two known spiked triangular compounds: $H_4Re_4(CO)_{15}^{2-}$ (3.288 Å) [14] and $H_4Re_4(CO)_{15}I^-$ (3.35 Å) [15]. It is also much longer than the other Re–Re distances in **3** and **4**. This long bond distance is comparable to that in $HRe_3(CO)_{14}$ [24]. Hence, one expects the nature of the bonding between Re4–Re1 must be similar to that in $HRe_3(CO)_{14}$.

The three phosphorus atoms in the tripod ligand are coordinated to Re2, Re3, and Re4 with bond distances of 2.497, 2.459 and 2.451 Å, respectively. An electron count on Re4 adds up to 16e only. Closer examination reveals that one of the phenyl group bonded to P2, locates at the vacant octahedral coordination site of Re4. Though the Re–C25 (2.532 Å) and Re–C30 (2.533 Å) distances are 0.26 Å

Table 5

Selected distances (Å) and angles (deg) of $H_4Re_4(CO)_{12}$(tripod)

Re1–Re2	3.237(2)	Re1–Re3	3.309(2)
Re1–Re4	3.435(2)	Re2–Re3	3.257(2)
P1–Re4	2.451(5)	P2–Re2	2.497(7)
P3–Re3	2.459(7)	Re4–C25	2.532(19)
Re4–C30	2.533(20)	C25–C30	1.360(32)
C25–C26	1.434(34)	C26–C27	1.359(25)
C27–C28	1.379(44)	C28–C29	1.326(54)
C29–C30	1.562(35)		
Re3–Re1–Re4	106.3(1)	Re2–Re1–Re4	92.8(1)
Re3–Re2–Re1	61.3(1)	Re2–Re1–Re3	59.7(1)
Re1–Re4–P1	95.2(1)	Re1–Re3–Re2	59.1(1)
Re3–Re2–P2	87.0(1)	Re1–Re2–P2	87.1(1)
Re2–Re3–P3	86.9(1)	Re1–Re3–P3	104.6(1)
P2–C49–P3	110.8(8)	P1–C49–P2	109.8(6)
P1–Re4–C10	88.1(6)	P3–C49–P2	119.8(8)
P1–Re4–C12	173.3(8)	P1–Re4–C11	94.3(7)
C11–Re4–C25	92.2(8)	C10–Re4–C25	163.7(8)
Re4–C25–C26	109.5(12)	C12–Re4–C25	110.9(9)
Re4–C30–C25	74.4(12)	Re4–C25–C3	74.5(11)
		Re4–C30–C29	110.5(13)

longer than those in the only X-ray characterized η^2,π-bonding in $(\eta^5\text{-}C_5Me_5Re(CO)_2)_2(\mu_2\text{-}\eta^2\eta'^2\text{-}C_6H_6)$ [25], inclusion of this double bond coordination makes the electron count on Re4 satisfy the 18e rule. More concrete evidence of C=C double bond coordination can be found in the C–C bond distance variation of the particular π-coordinating phenyl group. The C–C distances in the phenyl ring of C25 to C30 show distinctive nonequivalence. C25–C30 is 1.360 Å, which is typical for a C–C double bond length. C25–C26 and C29–C30 distances are 1.434 and 1.561 Å respectively, which are in the neighborhood of C–C single bond distance. But the C–C bond distances between C26–C29 again show delocalized double bond character. Hence, the coordination of C25–C30 double bond to Re4 is well supported. This is the first example of coordination of double bond in the phenyl group in tripod coordinated complexes. The long P2–Re2 bond distance, together with the long Re4–C25, Re4–C30 bond distances, indicate that there must be steric strain which prevents the achievement of optimal bond strength.

Although the hydrides in **3** and **4** have not been located by X-ray analysis, their positions can be inferred from their ^1H NMR chemical shifts. All hydrides are located in all available edge-bridging positions in **3** and **4**.

The PCP angle of tripod ligand can vary over a wide range as shown in Table 6. There is an obvious trend that as the M–M distance increases the PCP angle also increases as expected. And the M–M distances and PCP angle in $H_3Re_3(CO)_9$(tripod) are the largest among all known symmetrical $\eta^3\text{-}\mu_3$-tripod complexes. In the nonsymmetrical tripod complexes, the variation of the PCP angles is more complicated. For example, in $Pt(\eta^2\text{-tripod})_2^{2-}$ [10], besides a bit angle of 92.1°, the other two PCP angles are 120.0 and 120.1°. And in **4**, the three PCP angles are 109.4, 112.6 and 120.5°. Hence, it can be concluded that PCP angles in tripod complexes

Table 6

M–M distances and PCP angle of complexes with η^3-tripod ligand

Compound	M–M [a] (Å)	PCP [b] (deg)	Reference
$Fe(C_5H_5)(tripod)PF_6$	–	88	9
$Co_4(CO)_9(tripod)$	2.207	104.8	12a
$Co_4(CO)_6(tripod)(toluene)$	2.447	102.7	26
$Co_4(CO)_8(tripod)(PMe_3)$	2.484	103.6	27
$Co_4(CO)_7(tripod)(dppm)$	2.447	104.8	27
$Co_4(CO)_7(tripod)(PMe_3)_2$	2.463	105.0	27
$Ru_4(CO)_8(tripod)(P(OEt)_3)$	2.758	106.3	12b
$H_3Re_3(CO)_9(tripod)$	3.271	109.9	This work

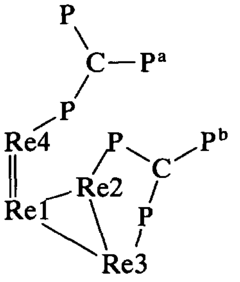
[a] Average distances between tripod coordinated metal atoms. [b] Averaged angle.

are flexible. The tripod ligand can adjust itself to the required geometry; the maximum angle seems to be around 120°.

In Table 1, it is noteworthy that in the tripod ^{31}P NMR spectra of **1–4**, the splitting due to $^2J(PP)$ is not observed except splittings between a pair of phosphorus atoms in **4**. There are precedents that some tripod complexes show the absence of $^2J(PP)$ [5] and some exhibit large $^2J(PP)$ [7b,8,10]. The reason for the variation in $^2J(PP)$ is not known. The ^1H NMR of tripod methine group also show interesting coupling pattern variation among **1–4**. Consistent with the proposed structure of **1**, the methine proton NMR signal is a triplet of doublet with very different coupling constants of 11.74 and 2.0 Hz, respectively. In **2**, the methine proton shows a triplet due to coupling to two equivalent phosphorus atoms. The coupling to the third phosphorus atom is not detectable. This is not surprising since the coupling constant may be less than the smaller coupling constant of 2.0 Hz in **1**. In **3**, as expected from the symmetry of the compound, a quartet splitting pattern is observed. And in **4**, complicate multiplet is observed because of the nonequivalence of all three phosphorus atoms. The variation of the coupling constant between methine proton and phosphorus atom $^2J(PH)$ should be sensitive to the *s* characters of the intervening chemical bonds. In turn, the P–C–P and P–C–H angles around methine carbon should influence the *s* characters. According to the conclusion that the PCP angles of tripod are flexible, therefore $^2J(PH)$ can vary over a wide range.

When **3** is heated under refluxing decane for 3 h, no change can be detected by NMR. Under identical reaction conditions, substantial amount of the uncapped $H_3Re_3(CO)_{12}$ is converted to $H_4Re_4(CO)_{12}$. Hence, despite the strains exhibited in its structure, capping by tripod yields cluster **3** with improved stability. The hydride ^1H NMR of **3** exhibits a quartet pattern instead of the expected triplet due to coupling to two nearby phosphorus atoms. This quartet pattern can be due to the presence of extra hydride coupling to the third phosphorus atom with a coupling constant which is accidentally equal to the hydride coupling constant to the two nearby phosphorus atoms. This is unlikely, because coupling constant is severely attenuated as the number of intervening chemical bonds increases. The other explanation is that the hydrides are moving rapidly among the three equivalent sites, probably through intermediate with terminal hydrides. Therefore, hydride coupling to all three phosphorus atoms can be observed. At low temperature (180 K), the quartets are still discernible. It indicates that this hydride motion is a low barrier process if it exists. Since, the hydrides in $H_3Re_3(CO)_{11}(PPh_3)$, $H_2Re_3(CO)_{10}(PPh_3)_2^-$ and $H_3Re_3(CO)_9(PPh_3)_3$, do not exhibit any fluxional behavior, the presence of a low barrier process in hydride motion is unreasonable. Therefore, the most likely explanation for the presence of quartet is that it is due to virtual coupling [28].

Under the reaction conditions of eq. 1, isolated **4** does not decompose to generate **1**, **2** and **3**. Likewise, **1**, **2** and **3** are also stable. And at high ratio of tripod to $H_4Re_4(CO)_{12}$ (8/1 molar ratio) under refluxing CH_2Cl_2, **1** and **3** are detected to be the major products with minor amount of **4**. With more rigorous conditions of refluxing $CHCl_3$ and high ratio of tripod to $H_4Re_4(CO)_{12}$ (25/1 molar ratio), the reaction proceeded rapidly, and **1** and **3** were the sole products. These results hinted that **1**, **2** and **3** are formed through an intermediate with more than one tripod ligand coordinated to $H_4Re_4(CO)_{12}$. A likely intermediate **5** with two tripod ligands coordinated to $H_4Re_4(CO)_{12}$, has a structure similar to **4**.



(**5**)

Coordination of P^a to Re4 and P^b to Re1 concomitantly, would give **1** and **3**. On the other hand, coordination of P^a to Re1 would give two molecules of $H_2Re_2(CO)_6(\eta^2\text{-}\mu_2\text{-tripod})$, which can further be transformed into **2**, or reacts bimolecularly to form **1** and **3**. Reaction of **1** or tripod with **5** to form **1**, **2** and **3** is also another possibility.

Supplementary material available. Tables of fractional atomic coordinates of all atoms, thermal parameters, complete sets of bond distances and bond angles, and figures of complete numbering schemes of **3** and **4**.

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