Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE X-RAY STRUCTURE OF TRIHYDRIDOBIS(1,2-BISDIPHENYLPHOSPHINOETHANE)RHENIUM(III), $ReH_3(DPPE)_2$

VINCENZO G. ALBANO and PIER LUIGI BELLON
Istituto di Chimica Generale ed Inorganica, Università di Milano, via G. Venezian, 21, 20133 Milano (Italy)

(Received October 4th, 1971)

SUMMARY

Trihydridobis(1,2-bisdiphenylphosphinoethane)rhenium(III), $ReH_3(DPPE)_2$ crystallizes in the space group $P2/c$, $Z=2$, with cell dimensions $a=16.09(2)$, $b=10.27(1)$, $c=19.11(2)$ Å, $\beta=128.0(1)°$. The data were collected photographically and 656 non-zero reflections were used to solve the structure by the heavy atom method ($R=0.075$). The $Re(DPPE)_2$ moiety has crystallographic C_2 symmetry and geometrical considerations together with potential energy computations allow to assign unequivocally the most favourable positions to the hydrido ligands. These occupy three equatorial positions of a slightly distorted pentagonal bipyramid. A comparative discussion of the structures of $ReH_3(DPPE)_2$ and $ReH_3(PPh_3)_2(DPPE)$ confirms the assignment of the hydrido ligand positions in both crystal species.

INTRODUCTION

Several rhenium complexes containing both hydrido and phosphine ligands have been described[1-4]. Structural data are available only for the compound $ReH_3(PPh_3)_2(DPPE)$[5,6]. In this complex a complete structure determination by X-ray diffraction allowed the determination of all the atomic postions except those of the hydrido ligands. Taking advantage of the molecular overcrowding, it was possible to draw indirect conclusions about the positions of these ligands from stereochemical considerations and potential energy computations. A map of the total energy was computed for all the non-bonding interactions of a hydrido ligand scanning a spherical surface centred at the rhenium atom. The Re–H distance of 1.68 Å (the same as found in the $[ReH_9]^{2-}$ anion[7]) was chosen as the radius of the sphere. The map showed only three energy minima, in which the hydrogen atoms were assumed to lie.

When suitable crystal samples of the complex $ReH_3(DPPE)_2$ became available, its structure was determined in order to provide further information on the stereochemistry of these hepta-coordinated species.

EXPERIMENTAL

Crystal data

The compound $ReP_4C_{52}H_{51}$, $M=986$, gives yellow monoclinic crystals. The

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS MODULI IN ELECTRONS FOR $ReH_3(DPPE)_2$

K	L	FO	/FC/
H = 0			
3	0	150	152
6	0	220	232
8	0	97	102
2	1	112	137
6	1	88	80
6	1	96	91
7	1	34	66
8	2	83	81
6	2	83	88
0	2	128	128
1	3	59	60
2	3	80	89
3	3	97	104
6	3	37	31
7	3	110	106
0	3	123	119
1	4	185	182
4	4	116	114
1	4	122	121
2	5	50	61
5	5	115	125
8	5	110	120
4	5	58	50
0	6	184	179
1	6	136	110
3	6	103	108
4	6	127	128
1	7	91	93
2	7	134	128
3	7	87	85
0	8	151	159
1	8	118	117
3	8	61	59
4	8	95	93
1	9	49	65
2	9	87	83
3	9	53	67
0	10	62	75
1	10	58	63
3	10	35	38
4	10	72	74
1	11	67	53
2	11	39	73
3	11	69	73
0	12	206	92
2	12	37	67
4	12	78	77
2	13	89	92
0	14	76	77
H = 1			
3	0	119	133
4	0	153	142
5	0	74	68
2	1	186	168
3	1	92	109
3	-1	81	107
5	1	100	111
6	-1	102	90
6	1	101	95
7	1	61	69
2	-2	109	74
3	2	96	94
3	-2	68	83
4	2	82	94
4	-2	133	133
0	2	112	110
5	-2	96	93
1	3	89	86
3	3	84	83
2	-3	101	100
3	3	96	97
3	-3	117	137
4	3	51	49
4	-3	39	44
6	3	94	87
6	-3	92	88
7	3	93	94
7	-3	113	108
0	4	66	68
0	-4	180	180
1	4	97	127
1	-4	164	152
2	4	76	61
4	4	118	117
4	-4	114	116
1	5	121	110
1	-5	32	22
2	5	118	116
2	-5	143	153
3	5	77	70
3	-5	104	102
5	-5	57	57
0	6	137	133
0	-6	178	174
1	6	51	63
1	-6	104	114
3	6	116	109
3	-6	61	57
4	6	85	83
4	-6	117	107
1	7	123	122
1	-7	113	106
2	7	118	112
2	-7	148	145
3	7	66	53
3	-7	103	98
0	8	54	50
0	-8	169	164
1	8	50	62
1	-8	71	87
3	8	56	53
3	-8	97	91
4	8	74	70
4	-8	121	120
1	-9	60	68
2	-9	139	136
3	-9	96	100
0	-10	99	96
1	-10	79	83
4	-10	82	80
1	-11	67	66
2	-11	79	80
3	-11	77	76
0	-12	109	95
1	-12	67	69
4	-12	84	84
2	-13	95	97
0	-14	90	100
2	-15	67	83
H = 2			
3	0	101	107
4	0	91	91
1	1	137	167
2	1	125	132
2	-1	131	145
3	1	91	92
3	-1	63	61
5	-1	51	61
6	1	74	82
6	-1	72	65
7	1	56	54
0	2	56	44
1	2	38	46
2	2	44	46
3	2	59	55
3	-2	99	92
4	2	64	78
4	-2	87	88
5	2	72	68
1	3	98	106
2	3	107	96
2	-3	53	76
3	3	71	70
3	-3	109	105
4	3	63	47
4	-3	46	43
6	3	74	84
6	-3	90	76
7	3	80	69
7	-3	76	63
1	4	51	36
1	-4	35	0
2	4	61	37
3	4	58	53
3	-4	43	34
4	4	83	78
4	-4	74	80
1	5	145	139
1	-5	130	124
2	5	119	110
2	-5	134	130
3	-5	91	97
4	-5	57	52
0	6	104	111
0	-6	104	98
1	6	50	47
1	-6	132	127
3	6	67	74
3	-6	82	77
4	6	65	64
4	-6	125	109
1	7	52	56
1	-7	116	100
2	7	98	84
2	-7	150	139
3	7	63	56
3	-7	78	80
0	-8	174	171
1	-8	67	64
3	-8	113	112
4	-8	100	99
1	-9	75	80
2	-9	122	119
3	-9	66	74
0	-10	70	83
1	-10	90	89
4	-10	70	78
2	-11	68	69
3	-11	86	95
0	-12	66	70
4	-12	83	81
2	-13	85	92
0	-14	89	93
2	-15	67	81
0	-16	75	77
H = 3			
0	0	50	69
1	0	96	89
2	0	39	22
3	0	77	79
4	0	74	89
7	0	63	58
1	-1	119	137
2	1	74	87
2	-1	110	98
3	1	69	62
3	-1	64	72
5	-1	71	83
6	1	74	72
6	-1	44	59
0	2	77	87
1	2	32	46
3	-2	67	74
4	-2	78	74
5	2	68	59
1	3	38	43
2	3	48	61
2	-3	94	94
3	-3	35	42
6	-3	39	81
0	4	94	93
0	-4	193	162
3	4	81	72
3	-4	59	62
4	4	65	64
1	5	68	62
1	-5	30	29
2	5	108	105
3	5	83	68
3	-5	62	70
4	-5	63	56
0	6	130	118
0	-6	229	202
1	6	50	47
1	-6	139	130
3	6	73	67
3	-6	53	46
4	6	76	74
4	-6	127	118
1	-7	134	119
2	7	62	67
2	-7	107	109
3	-7	69	57
0	-8	132	121
1	-8	38	45
3	-8	126	115
4	-8	65	63
1	-9	66	63
2	-9	85	89
0	-10	77	80
1	-10	56	61
3	-10	76	72
4	-10	59	62
2	-11	44	47
3	-11	75	76
4	-12	81	68
2	-13	56	52
0	-14	67	82
2	-15	73	73
H = 4			
0	0	47	40
1	0	97	111
2	0	52	41
3	0	36	38
4	0	50	52
5	0	80	78
1	-1	43	55
2	1	66	64
2	-1	86	97
3	1	48	57
4	-1	49	49
5	-1	56	64
6	1	76	83
7	1	47	75
0	2	63	84
0	-2	227	222
1	2	43	34
3	-2	53	50
4	2	81	82
4	-2	82	92
5	2	78	71
1	-3	102	103
2	3	60	62
2	-3	100	91
3	-3	37	31
4	-3	61	54
5	-3	86	77
0	4	126	139
0	-4	145	119
1	4	83	78
1	-4	157	169
3	4	55	70
3	-4	97	79
4	4	72	70
4	-4	62	76
1	5	76	65
2	5	81	87
2	-5	113	107
3	-5	46	61
0	6	105	112
0	-6	80	59
1	6	74	76
3	6	72	60
4	6	80	73
4	-6	61	66
1	-7	59	69
2	7	51	56
2	-7	70	62
0	-8	128	126
3	-8	79	74
4	-8	74	72
1	-9	76	87
2	-9	73	81
0	-10	61	71
0	-10	44	81
1	-10	57	63
3	-10	70	69
4	-10	76	73
1	-11	43	34
2	-11	64	57
4	-12	46	43
2	-15	66	71
H = 5			
0	0	54	54
1	0	135	132
2	0	74	56
4	0	74	72
5	0	100	105
8	0	67	72
1	-1	75	83
2	1	59	66
2	-1	97	120
3	1	94	96
3	-1	43	49
6	1	73	74
8	-1	58	61
7	1	97	98
0	2	71	72
0	-2	204	216
1	2	48	58
1	-2	37	39
3	-2	75	87
4	2	104	100
4	-2	90	93
5	2	62	67
1	3	74	77
1	-3	124	122
2	3	93	93
2	-3	119	127
3	-3	53	54
5	-3	70	71
0	4	113	119
0	-4	102	109
1	4	73	74
1	-4	106	107
3	4	88	84
3	-4	58	63
4	4	69	72
4	-5	100	96
1	5	79	84
1	-5	142	144
2	5	103	98
2	-5	115	124
3	-5	89	83
0	6	96	80
0	-6	55	51
1	6	55	69
1	-6	43	39
4	6	87	80
4	-6	91	86
2	-7	87	88
3	-7	41	36
0	8	88	74
0	-8	83	58
1	-8	88	91
4	-8	69	61
1	-9	98	93
2	-9	83	85
3	-9	53	45
0	-10	68	80
4	-10	72	75
1	-11	58	65
2	-11	80	82
1	-12	42	42
4	-13	49	48
2	-15	69	68
0	-16	64	69
H = 6			
0	0	64	70
1	0	100	95
3	0	59	59
4	0	85	91
6	0	88	98
8	0	70	77
1	1	56	62
1	-1	37	48
2	1	88	86
2	-1	130	120
3	1	67	82
3	-1	116	136
4	1	61	59
4	-1	44	42
6	1	59	76
6	-1	112	98
0	2	99	95
0	-2	153	157
1	2	74	80
1	-2	83	85
3	-2	99	99
4	2	69	81
4	-2	107	109
1	3	77	76
1	-3	113	124
2	3	109	99
2	-3	132	132
3	3	85	71
3	-3	62	71
5	-3	79	73
0	4	147	138
0	-4	183	176
1	4	71	75
1	-4	113	115
3	4	84	78
3	-4	85	89
4	4	82	84
4	-4	82	87
1	5	83	95
1	-5	63	62
2	5	100	99
2	-5	119	109
3	5	76	77
3	-5	104	107
0	6	70	62
0	-6	151	160
1	-6	105	110
3	-6	57	47
4	-6	84	97
1	7	64	38
1	-7	64	74
2	-7	90	84
3	-7	87	98
4	-7	65	62
0	-8	65	74
1	-8	85	81
4	-8	74	75
1	-9	89	73
2	-9	134	121
3	-9	63	67
0	-10	117	105
1	-10	75	67
3	-10	87	94
4	-10	89	82
1	-11	54	62
2	-11	93	88
3	-11	64	65
0	-12	92	90
1	-12	76	75
4	-12	63	67
1	-13	56	53
2	-13	51	52
4	-14	59	62
2	-15	59	70
0	-16	72	81
2	-17	57	65
H = 7			
0	0	99	100
1	0	65	71
3	0	56	52
4	0	71	87
5	0	85	90
1	1	53	60
1	-1	58	60
2	1	103	101
2	-1	94	95
3	1	78	82
3	-1	73	80
6	-1	80	76
0	2	112	107
0	-2	133	127
1	2	66	71
1	-2	104	122
3	-2	63	63
4	2	80	86
4	-2	84	91
1	3	86	86
1	-3	76	74
2	3	106	95
2	-3	114	117
3	-3	102	97
0	4	92	91
0	-4	200	199
1	-4	84	80
3	-4	95	106
4	-4	131	128
1	-5	76	76
2	-5	126	139
3	-5	120	111
0	-6	125	110
1	-6	109	110
3	-6	59	61
4	-6	89	84
1	-7	28	22
2	-7	68	74
3	-7	98	94
4	-7	63	53
0	-8	100	90
1	-8	67	64
4	-8	97	97
1	-9	89	82
2	-9	90	92
3	-9	85	79
0	-10	248	236
1	-10	134	130
3	-10	108	100
4	-10	111	100
1	-11	101	86
2	-11	153	155
3	-11	85	80
0	-12	84	78
1	-12	84	80
3	-12	73	64
4	-12	75	78
1	-13	41	47
0	-14	78	76
1	-14	59	57
4	-14	62	75
2	-15	65	74
0	-16	77	84
2	-17	64	79
0	-18	73	83
H = 8			
0	0	67	72
4	0	64	80
5	0	65	63
8	0	72	67
1	1	57	70
1	-1	46	50
2	1	70	79
2	-1	74	77
0	2	92	98
1	2	57	63
1	-2	69	78
4	-2	60	65
1	-3	90	99
2	-3	102	103
3	-3	50	55
0	-4	141	144
1	-4	38	33
3	-4	80	82
4	-4	104	107
1	-5	73	72
2	-5	115	113
3	-5	72	79
0	-6	73	69
1	-6	100	97
3	-6	48	49
4	-6	84	85
1	-7	43	41
2	-7	73	81
3	-7	84	80
4	-7	52	44
0	-8	72	75
1	-8	69	75
4	-8	94	92
1	-9	57	55
2	-9	100	102
3	-9	77	77
0	-10	152	138
1	-10	62	58
3	-10	74	63
4	-10	100	93
1	-11	115	117
2	-11	140	133
3	-11	83	78
0	-12	131	128
1	-12	80	79
4	-12	93	99
2	-13	90	99
3	-13	90	77
0	-14	72	71
1	-14	65	65
2	-15	72	73
0	-16	68	78
4	-16	58	60
2	-17	86	89
0	-18	74	79
H = 9			
2	1	58	65
1	-2	49	49
1	-3	56	50
2	-3	62	62
0	-4	111	110
1	-4	48	35
4	-4	61	56
1	-5	160	91
2	-5	78	80
0	-6	52	40
1	-6	49	50
3	-6	64	69
4	-6	56	60
1	-7	46	42
2	-7	65	65
3	-7	76	75
4	-8	64	69
1	-9	42	54
2	-9	79	80
3	-9	43	50
0	-10	75	67
1	-10	58	56
3	-10	65	70
4	-10	69	64
1	-11	76	67
2	-11	92	84
3	-11	60	56
0	-12	126	122
3	-12	59	61
4	-12	84	81
2	-13	72	80
2	-15	52	60
0	-16	74	60
4	-16	67	63
2	-17	71	77
0	-18	71	79
H = 10			
0	0	62	60
0	-5	78	70
1	-5	55	56
2	-5	66	69
0	-6	68	73
1	-6	45	41
1	-7	50	49
1	-10	49	53
1	-11	62	62
2	-11	62	66
0	-12	86	69
3	-12	63	65
4	-12	60	53
0	-16	57	57
2	-17	35	63
0	-18	62	58
H = 11			
0	0	73	68
0	-4	62	60
0	-6	90	92
0	-12	70	65
H = 12			
0	-6	102	94
0	-12	65	66
0	-14	56	55
H = 13			
0	-6	94	91
0	-8	48	56
0	-12	57	64
0	-14	68	76
H = 14			
0	-6	101	66
0	-8	67	59
0	-12	61	55
0	-14	82	74
H = 15			
0	-8	77	68
0	-14	45	60

crystal data are $a = 16.09(2)$, $b = 10.27(1)$, $c = 19.11(2)$ Å, $\beta = 128.0(1)°$, $U = 2487$ Å^3, $D_m = 1.33(2)$, $D_c = 1.31$ g/cm^3, $Z = 2$, Cu-K_α radiation $\lambda = 1.5418$ Å. From systematic extinctions ($h0l$ with l odd) two space groups were possible, Pc and $P2/c$. Data collected on Weissenberg integrating camera, multiple films, measured photometrically. Two intersecting sets of data were collected with different crystals along the axes [001] and [010]. After correction for the Lorentz, polarization, and absorption effects ($\mu = 66$ cm^{-1}), and after merging the two sets of reflections, 656 independent nonzero F_0's were obtained.

Determination and refinement of the structure

A tridimensional Patterson map allowed determination of the positions of the rhenium and phosphorus atoms. The rhenium coordinates 0, 0.12, 0.25 indicated clearly that this atom was in the special position e of the space group $P2/c$. The site symmetry of this position is C_2, consequently only one half of the molecule is crystallographically independent. Together with the rhenium atom one hydrido ligand should lie on the symmetry axis. With this choice of space group, the structure was successfully refined by least squares up to a conventional R factor 0.075. This relatively high discrepancy index results from partial decomposition of the crystal within the X-ray beam. In the refinement the block-diagonal approximation of the normal matrix was used, the non-group atoms in 4 × 4 blocks and the phenyl rings—treated as rigid groups of D_{6h} symmetry, C–C = 1.392 Å—in 7 × 7 blocks (see details in ref. 8). The weighting scheme adopted was $w = 1/(30 + 0.1|F_0| + 0.001|F_0|^2)$, the coefficients of the polynomial were chosen in order to obtain an approximately constant distribution of the quadratic error $w\Delta F_0^2$ over the entire range of F_0's. The structure factors and least squares computations were based upon the atomic scattering factors of Cromer and Mann[9]. A final difference Fourier revealed one signal of about 2 electrons per Å^3 at the position of the rhenium atom. This effect was probably due to the fact that the Fourier summation did not include the imaginary contribution from the anomalous scattering of rhenium. All the remaining signals were in the range ±0.5 e^-/Å^3 and did not reveal significant features. The results of the refinement are reported in Tables 1–3. Table 1 gives a list of the observed and calculated structure factors moduli, and in Tables 2 and 3 the final parameters of the atoms are reported.

Computations

All the computations were carried out on an IBM 7040 computer. Data

TABLE 2

POSITIONAL[a] AND THERMAL PARAMETERS FOR NONGROUP ATOMS WITH ESTIMATED STANDARD DEVIATIONS

	x/a	y/b	z/c	B (Å^2)
Re	0	1208(3)	2500	1.9(2)
P_1	1535(8)	977(15)	2630(7)	2.6(3)
P_2	−758(9)	1772(13)	1028(7)	2.6(3)
C_1	1274(30)	1634(32)	1593(28)	5.0(8)
C_2	114(29)	1233(37)	783(23)	5.9(8)

[a] All values × 10^4.

TABLE 3

DERIVED POSITIONAL PARAMETERS OF PHENYL CARBON ATOMS REFINED AS RIGID GROUPS[a,b,c]

	x/a	y/b	z/c		x/a	y/b	z/c
C_3	2040	−665	2652	C_{15}	−2039	1008	73
C_4	2691	−899	2416	C_{16}	−2971	1711	−482
C_5	3052	−2155	2470	C_{17}	−3911	1066	−1115
C_6	2765	−3176	2760	C_{18}	−3919	−282	−1193
C_7	2113	−2941	2996	C_{19}	−2987	−985	−637
C_8	1751	−1686	2942	C_{20}	−2047	−341	−4
C_9	2751	1884	3484	C_{21}	−964	3491	608
C_{10}	3722	1265	4054	C_{22}	−1277	3694	−243
C_{11}	4598	1959	4739	C_{23}	−1382	4958	−594
C_{12}	4503	3274	4856	C_{24}	−1175	6016	−13
C_{13}	3531	3893	4287	C_{25}	−863	5811	838
C_{14}	2655	3198	3602	C_{26}	−759	4550	1149

[a] All values × 10^4.

[b] Mean estimated standard deviations 0.003.

[c] Isotropic temperature factors of the phenyl rings: 6.4, 6.3, 6.0, 6.5; estimated standard deviation 0.6.

reduction and absorption corrections were based upon our Fortran programmes. For Fourier analyses, structure factors and least squares, local versions were used of the following entries in the 1966 "International World List of Crystallographic Programs"; 7528, 7531, 7532, and 7535. A programme written by Domenicano and Vaciago of the University of Rome was used in the computation of the molecular parameters.

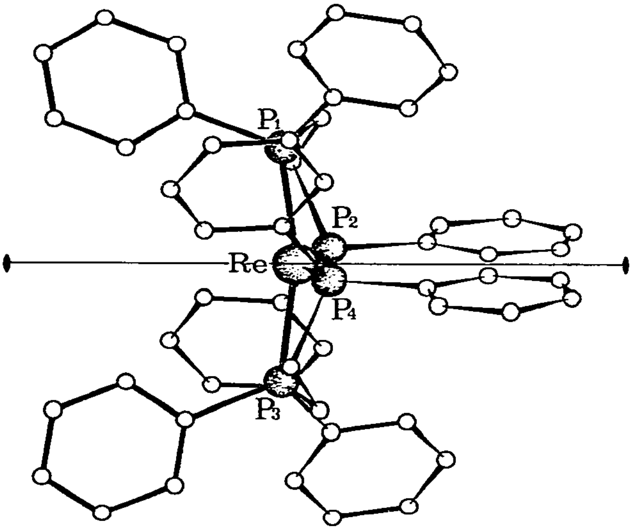
DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A perspective view of the molecule is given in Fig. 1 and the most significant distances and angles are reported in Table 4. The stereochemistry of the ReP_4 group in this complex is similar to that found in $ReH_3(PPh_3)_2$(DPPE) but with some significant differences in the P–Re–P angles. An analysis of these differences (see Table 4), together with the constraints imposed by the molecular C_2 symmetry of the present complex, allows a more definite assignment of the hydrido ligand positions. In the complex $ReH_3(PPh_3)_2$(DPPE), on the basis of the potential energy calculations, two hydrogen atoms were expected to lie in the Re, P_2, P_4 plane (toward the left in Fig. 1); the third one was expected to lie above this plane in a position surrounded by atoms Re, P_1, P_2, and P_4 (upper right sector in Fig. 1). In the present complex the P_2–Re–P_4 angle is 25° wider than in $ReH_3(PPh_3)_2$(DPPE); this fact strongly suggests that the third hydrido ligand (H_1 in Fig. 2) does now lie in the Re, P_2, P_4 plane and occupies the required special position on the twofold axis. This rearrangement allows a further opening of the P_1–Re–P_3 angle. The two first hydrido ligands, which are now related by the twofold axis, probably occupy essentially the same positions as they do in the coordination sphere of the complex $ReH_3(PPh_3)_2$(DPPE). The large widening of the P_2–Re–P_4 angle might, however, push them significantly out of the Re, P_2, P_4 plane. On the basis of these considerations the co-ordina-

TABLE 4

BOND DISTANCES (Å) AND RELEVANT ANGLES (°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR THE COMPLEX $ReH_3(DPPE)_2$. SOME CORRESPONDING VALUES FOR $ReH_3(PPh_3)(DPPE)$ ARE SHOWN IN SQUARE BRACKETS

$Re-P_1$	2.34(2)		$Re-P_1-C_3$	121(1)
$Re-P_2$	2.35(2)		$Re-P_1-C_9$	121(1)
P_1-C_3	1.86(4)		$Re-P_2-C_{15}$	121(1)
P_1-C_9	1.85(4)		$Re-P_2-C_{21}$	125(1)
P_2-C_{15}	1.89(5)		$Re-P_1-C_1$	108(1)
P_2-C_{21}	1.88(4)		$Re-P_2-C_2$	109(1)
P_1-C_1	1.88(4)		$P_1-C_1-C_2$	108(2)
P_2-C_2	1.82(5)		$C_1-C_2-P_2$	108(2)
C_1-C_2	1.58(6)		$C_3-P_1-C_9$	103(2)
P_1-Re-P_3	167.4(5)	[159.1]	$C_9-P_1-C_1$	100(2)
P_2-Re-P_4	151.5(5)	[126.9]	$C_1-P_1-C_3$	99(2)
P_1-Re-P_4	99.4(5)	[99.2]	$C_{15}-P_2-C_{21}$	100(2)
P_1-Re-P_2	83.6(5)	[81.4]	$C_{21}-P_2-C_2$	98(2)
			$C_2-P_2-C_{15}$	100(2)



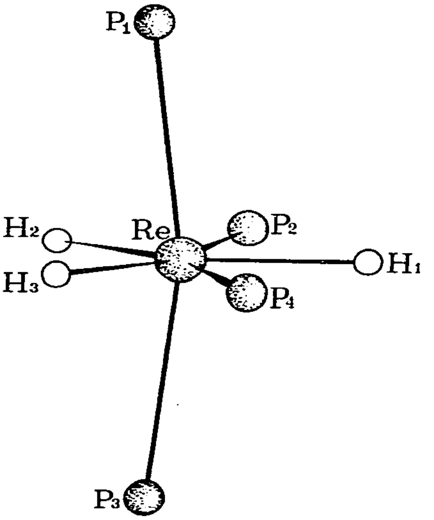


Fig. 1. A perspective view of the $ReH_3(DPPE)_2$ molecule. Only the rhenium, phosphorus, and carbon atoms are shown.

Fig. 2. The inner coordination sphere of the molecule with the hydrido ligands in their "ideal" positions. The twofold axis passes through the Re and H_1 atoms.

tion pattern around the metal atom is essentially that of a pentagonal bipyramid; Fig. 2. shows this idealized structure for the ReH_3P_4 moiety.

The geometric considerations just described have been confirmed by computation of a potential energy map for the H-H[10], (assuming the hydrogen atoms of C_6H_5 and C_2H_4 groups to lie at 1.08 Å from the corresponding carbon atoms, with

C–C–H angles of 120° and 109.5° respectively), H–C[11] and H–P[12] non bonding interactions. A potential well has been found in the position postulated for the H_1 atom. However the well is symmetrically diffused for about 20° above and below the equatorial plane. In spite of this result a disordered distribution of the H_1 atom around the special position is not probable because no induced disorder on the neighbouring atoms has been detected. Another wide potential minimum is present in the zone in which H_2 and H_3 are thought to be. If the mutual interaction between the H_2 and H_3 atoms is taken into account the minimum splits into two wells whose minima form an angle at the metal of about 75°; the dihedral angle between the plane containing the two minima and the rhenium atom and the Re. P_2, P_4 plane is about 7°. This result indicates that H_2 and H_3 can, indeed, lie out of the equatorial plane.

Although the potential energy computations are necessarily approximate, they do indicate that only one spatial distribution of the hydrido ligands is possible, other conformations being forbidden by steric hindrance from the phosphine ligands. Lastly, we note that similarities and differences between the geometries of the present complex and that of $ReH_3(PPh_3)_2(DPPE)$ mutually confirm the assignments of the hydrido ligand positions in both structures.

The most important bond distances found in this structure are those for the Re–P bonds, which are both 2.34(2) Å long. The corresponding values in $ReH_3(PPh_3)_2(DPPE)$ are in the range 2.36–2.39 Å with a mean of 2.37 Å. These distances are significantly shorter than those found in other rhenium complexes in which the mean Re–P value is 2.46 Å (see ref. 13 and references therein). The difference can be explained by a more pronounced π character of the Re–P bonds in these compounds, in which the phosphorus atoms are the only ligands with π accepting ability.

As for the geometry of the phosphinic ligands, the bond parameters reported in Table 4 are normal values. The conformation of the chelate ring is described in Table 5 by means of the torsion angles whose values are in the range of those reported in ref. 14.

TABLE 5

THE CONFORMATION OF THE FIVE-MEMBERED CHELATE RING INVOLVING THE RHENIUM ATOM AND THE BIDENTATE DIPHOSPHINE LIGAND. THE VALUES GIVEN ARE THE TORSION ANGLES (°) ABOUT SUCCESSIVE BONDS IN THE RING

$\tau(Re–P_1)$	9.3	$\tau(P_1–C_1)$	−38.6
$\tau(C_1–C_2)$	53.0	$\tau(C_2–P_2)$	−45.3
$\tau(P_2–Re)$	17.0		

ACKNOWLEDGEMENTS

This research has been supported by the Italian National Research Council (CNR). We thank M. Freni, who also supplied the crystals, and V. Scatturin for useful discussions.

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