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The Crystal Structure of a Trinuclear Transition Metal Carbonyl Hydride: $HRe_2Mn(CO)_{14}$

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Received May 18, 1967

The crystal and molecular structure of dirhenium manganese tetradecacarbonyl hydride, $HRe_2Mn(CO)_{14}$, has been determined by X-ray diffraction techniques, the final R factor being 10.4% for complete three-dimensional data ($\sin \theta_{max} = 0.38$; Mo Kα radiation) collected with an automated diffractometer. The compound crystallizes in space group $P2_1/n$ (C_{2h}^5; No. 14) with $a = 9.31 \pm 0.01$ A, $b = 15.82 \pm 0.02$ A, $c = 14.38 \pm 0.02$ A, $\beta = 106° 25' \pm 5'$, $Z = 4$. The observed and calculated densities are 2.64 ± 0.05 and 2.68 g cm^{-3}, respectively. The molecule adopts a *cis* configuration, the angle at the central rhenium atom, $\angle(Re_1 \cdots Re_2—Mn)$, being 98.1°. The rhenium–manganese distance of 2.960 ± 0.003 A is in substantial agreement with the metal–metal bond lengths in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, but the rhenium–rhenium distance of 3.392 ± 0.002 A is some 0.37 A longer than anticipated for a simple σ bond. These observations, coupled with the symmetrical arrangement of carbonyl groups about each metal, lead to the proposal that the hydrogen atom is situated between the two rhenium atoms, forming a two-electron, three-center bond. The carbonyl groups in the $(OC)_4Re–Mn(CO)_5$ portion of the molecule are staggered, whereas those in the hydrogen-bridged portion of the molecule are in the eclipsed configuration.

Introduction

Mononuclear hydrides of transition metals have been known since 1931,[2] but unambiguous evidence that the hydride ligand occupies a regular stereochemical position in the metal coordination sphere was first obtained[3] only comparatively recently. A number of mononuclear transition metal hydrides have been examined by X-ray diffraction,[3–10] neutron diffraction,[11] and broad-line nmr techniques,[12–14] but there are still some discrepancies regarding the length of the metal–hydrogen bond. Polynuclear hydrides have not been so extensively studied, but X-ray diffraction studies of the complexes $HMn_3(CO)_{10}(BH_3)_2$,[15] $[\pi\text{-}C_5H_5\text{-}Mo(CO)_2]_2\{P(CH_3)_2\}\{H\}$,[16] and $[(C_2H_5)_3NH^+][HFe_3(CO)_{11}^-]$[17] indicate that they contain bent M–H–M bonds; the anion in $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ presumably contains a linear Cr–H–Cr bond.[18]

The present structural study of $HRe_2Mn(CO)_{14}$ was undertaken to determine the over-all molecular configuration and to ascertain (indirectly) the location of the hydrogen atom. A preliminary account of this work has been published.[19]

Unit Cell and Space Group

The compound was prepared by Fellmann[20] and supplied to us by Professor H. D. Kaesz. In the solid phase it is air stable and is not X-ray sensitive. Crystals are isolated as irregular platelike yellow parallelepipeds, the c axis being coincident with the long edge of the crystal and the b axis being perpendicular to the face of the plate. The crystals selected for the analysis were mounted on glass fibers and inserted into 0.2-mm diameter thin-walled capillary tubes.

Optical examination of the crystal and a reciprocal lattice symmetry of C_{2h} (2/m) indicated that the crystals belonged to the monoclinic system. Unit-cell parameters, calculated from calibrated ($a_{NaCl} = 5.640$ A) zero-level precession photographs taken with Mo Kα radiation (λ 0.7107 A) at 24 ± 2° are: $a = 9.31 \pm 0.01$ A, $b = 15.82 \pm 0.02$ A, $c = 14.38 \pm 0.02$ A, and $\beta = 106° 25' \pm 5'$. The unit cell volume is 2032 A^3. The observed density, obtained by flotation in a methyl iodide–bromoform mixture ($\rho_{obsd} = 2.64 \pm 0.05$ g cm^{-3}) is in satisfactory agreement with that calculated for $M = 820$ and $Z = 4$ ($\rho_{calcd} = 2.68$ g cm^{-3}).

The observed extinctions, $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, indicate that the space group is $P2_1/n$, a nonstandard setting of space group No. 14 (C_{2h}^5), having the following equipoints: x, y, z; $-x, -y, -z$; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$.

Collection and Reduction of X-Ray Diffraction Data

Data were collected with a 0.01°-incrementing Buerger automated diffractometer, used in conjunction with a fully stabilized Phillips X-ray generator (operated at

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[1] On leave from the Department of Chemistry, University of California, Los Angeles, Calif. 90024; supported by Grant GP-6720, from the National Science Foundation.

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47 kv/17 ma), a Phillips transistorized scintillation counter, and a Phillips electronics panel. The scintillation counter was adjusted to receive Mo Kα radiation (λ 0.7107 A), the Kβ component being virtually eliminated by the use of a 3.0-mil zirconium filter at the X-ray source. The base line of the pulse-height analyzer, the window voltage, and the countervoltage were maintained at constant values throughout the analysis. The diffractometer was accurately aligned by determining the counterangle (Υ) and crystal-rotation angle (ϕ) for some ten sets of zero-level reflections ($hk0$, $h\bar{k}0$, $\bar{h}k0$, and $\bar{h}\bar{k}0$) for the crystal under investigation. The diffractometer was programmed to collect all data in a given Weissenberg zone, using the standard "stationary background, ω-scan, stationary background" counting sequence. [The angle scanned, ω, is given by $\omega = (2.0 + 0.8/L)°$, where $1/L$ is the Lorentz factor. The inclusion of the term involving the Lorentz factor allows for the divergence of the X-ray beam, which manifests itself in extended low-order reflections on upper-level data.[21]] Within each zone, the over-all stability of the entire system was monitored by remeasuring a carefully preselected check reflection after every 20 reflections had been collected. [No significant, *i.e.*, $>3\sqrt{\text{count}}$, variation was detected.] Throughout the analysis, all scans were recorded on a chart recorder in order to keep a check on peak profile, centering of the reflection in ϕ, and possible overlap of adjacent reflections.

The intensity, $I(hkl)$, of a reflection hkl [having Weissenberg coordinates $\Upsilon_0(hkl)$ and $\phi_0(hkl)$] was recorded in the following manner: (i) The counter was positioned to $\Upsilon_0(hkl)$, where it remained during the subsequent steps. (ii) The crystal was rotated to an angle ϕ_1 [$= \phi_0(hkl) - \omega(hkl)/2$] and the first background, B_1, counted for t seconds. (iii) The crystal was slowly rotated by $\omega(hkl)$ degrees at a constant rate of 2°/min until it reached the angle ϕ_2 [$=\phi_0(hkl) + \omega(hkl)/2$]. The entire scan took $4t$ seconds, the integrated count being C. (iv) The second background, B_2, was measured for t seconds at ϕ_2.

Using equiinclination geometry, 2234 independent reflections from the zones $hk0$ through $hk14$ were collected from crystal I; this represents complete data to $\sin\theta = 0.38$. In order to correlate the c-axis data, levels $h0l$ through $h6l$ were collected from crystal II. A total of 120 reflections for which $I(hkl)$ [$=C - 2(B_1 + B_2)$] values were negative or zero, or for which the background counts were highly asymmetric, were omitted from the analysis. Observed reflections were weighted according to the following scheme [where δ is the maximum probable error ($=3\sigma$) in the counting statistics]

$$I(hkl) \geqslant \delta; \qquad \sigma(hkl) = 0.1I(hkl)$$

$$I(hkl) \leqslant \delta; \qquad \sigma(hkl) = 0.1\delta^2/I(hkl)$$

For Mo Kα radiation, the linear absorption coefficient (μ) is 132 cm^{-1}, making an absorption correction mandatory. Lorentz, polarization, and absorption corrections were applied to all data, using a local modification of the program GNABS.[22] For crystal I (0.19 × 0.10 × 0.28 mm, volume 0.00532 mm^3, mass 14.3 μg) transmission factors varied from 0.175 to 0.305; for crystal II (0.19 × 0.10 × 0.16 mm, volume 0.00332 mm^3, mass 8.9 μg) the variation was from 0.109 to 0.288. A least-squares analysis of common reflections was used to place the corrected intensity data on a common scale.[23] Finally, a Wilson plot was used to place the data on an approximately absolute scale and to determine the over-all thermal parameter (the value $\bar{B} = 2.72$ A^2 was found by this method).

Determination and Refinement of the Structure

The positions of the two rhenium atoms ($x_1 = 0.042$, $y_1 = 0.163$, $z_1 = 0.123$; $x_2 = -0.112$, $y_2 = 0.360$, $z_2 = 0.097$) were determined unambiguously from a three-dimensional Patterson synthesis[24] which had been sharpened so that the average intensity was independent of $\sin\theta$ and which had the origin peak reduced to the height of a single Re···Re interaction. A three-dimensional electron density map phased by the two rhenium atoms immediately revealed the position of the manganese atom ($x_{Mn} = -0.123$, $y_{Mn} = 0.383$, $z_{Mn} = 0.293$) and suggested some possible positions for the carbonyl groups. (These latter positions were temporarily ignored but later found to be consistent with true atomic positions.) The positions of the three metal atoms were not refined; three successive different Fourier syntheses, based on structure factor calculations[25] phased by an increasing number of atoms, led to the unambiguous location of all nonhydrogen atoms. Four cycles of least-squares refinement of positional and individual isotropic thermal parameters for all atoms resulted in the discrepancy index ($R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) converging from its initial value of 29.4% to a value of 13.2%. A difference Fourier at this stage indicated that the metal atoms were not adequately described by isotropic thermal parameters and anisotropic thermal parameters (T) in the form $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ were applied to the metals. [Since the standard deviations on the isotropic parameters of oxygen and carbon atoms were rather large (see Table II), it was thought that the use of anisotropic parameters for these atoms was not justifiable.] Four further cycles of refinement, varying anisotropic thermal parameters for the three metal atoms and positional parameters for all 31 atoms, led to the final discrepancy index, $R_F = 10.4\%$ for 2114 independent reflections, at which stage refinement was

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(21) D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

(22) GNABS is a general absorption-correction program for the IBM 7090, by C. W. Burnham.

(23) Scale factors for the various zones were computed by a least-squares method which minimizes a sum of residuals linear in the logarithms of the scale factors: A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(24) Patterson and Fourier syntheses were calculated using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090 by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende.

(25) Structure factor calculations and full-matrix refinement of positional and thermal parameters were performed using ORFLS, a FORTRAN crystallographic least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $HRe_2Mn(CO)_{14}$ (IN ELECTRONS)

H	K	FO	FC
L = 0			
2	0	322	250
4	0	-196	-159
6	0	-163	-131
8	0	27	10
2	1	133	103
3	1	259	206
4	1	-159	-129
5	1	171	137
6	1	-353	-295
8	1	-146	-153
9	1	-119	-111
2	2	-146	-124
3	2	-616	-533
4	2	-110	-97
6	2	33	38
7	2	46	38
8	2	38	30
9	2	-38	-49
1	3	-76	-71
2	3	234	175
3	3	-384	-325
4	3	51	50
5	3	-247	-226
6	3	-135	-113
7	3	67	63
8	3	148	149
0	4	-527	-479
1	4	129	122
2	4	-252	-214
3	4	194	171
4	4	248	215
5	4	222	182
6	4	107	97
7	4	70	65
8	4	-43	-46
9	4	25	25
1	5	342	282
2	5	-154	-140
4	5	82	68
5	5	-121	-90
6	5	271	250
7	5	18	13
8	5	162	149
0	6	304	293
1	6	229	185
2	6	280	247
3	6	222	186
5	6	-64	-55
6	6	-69	-58
7	6	-137	-120
8	6	-82	-76
2	7	-293	-251
3	7	158	122
4	7	-152	-136
5	7	208	184
6	7	-47	-40
7	7	-10	-13
8	7	-69	-95
0	8	128	98
1	8	-76	-73
2	8	-27	-29
3	8	-199	-195
4	8	-250	-211
5	8	-160	-140
6	8	-68	-54
7	8	-50	-43
8	8	87	86
1	9	-253	-225
2	9	226	211
3	9	-56	-42
4	9	49	39
6	9	-70	-81
0	10	-162	-154
1	10	-95	-70
2	10	-125	-118
3	10	-62	-46
5	10	127	119
6	10	68	63
7	10	159	144
1	11	174	159
2	11	135	122
4	11	88	78
5	11	-84	-75
6	11	60	51
0	12	14	3
1	12	59	50
2	12	106	100
3	12	77	66
4	12	125	116
5	12	22	21
1	13	71	60
2	13	-146	-133
4	13	-123	-113
5	13	25	9
1	14	23	12
4	14	-49	-39
1	15	-145	-133
3	15	-43	-45
2	16	-20	-26
L = 1			
-9	0	47	30
-7	0	133	117
-5	0	98	57
-3	0	135	96
5	0	-301	-269
7	0	-245	-220
-9	1	99	84
-8	1	-43	-26
-7	1	189	174
-6	1	65	62
-5	1	227	199
-4	1	226	201
-3	1	-40	-42
-2	1	342	247
2	1	-183	-138
3	1	30	27
4	1	-39	-32
6	1	116	100
7	1	-113	-107
8	1	-40	-62
9	1	-75	-63
-9	2	-23	-8
-8	2	93	76
-7	2	-57	-45
-5	2	-56	-43
-3	2	-251	-199
-2	2	117	114
2	2	-362	-353
3	2	-60	-28
4	2	-482	-437
5	2	73	77
6	2	-80	-71
7	2	62	58
8	2	119	118
9	2	44	41
-9	3	-37	-13
-8	3	62	58
-6	3	-113	-107
-5	3	106	95
-4	3	-446	-403
-3	3	90	21
-2	3	-373	-293
-1	3	-219	-182
0	3	-71	-56
1	3	-117	-91
2	3	161	138
3	3	167	139
4	3	-14	-18
5	3	139	119
6	3	-50	-40
7	3	-62	-62
8	3	79	83
-8	4	-89	-80
-7	4	-94	-91
-6	4	-101	-78
-4	4	-124	-90
-3	4	22	13
-2	4	-131	-104
-1	4	-109	-129
0	4	165	147
1	4	-349	-337
2	4	259	233
3	4	-110	-81
4	4	203	187
5	4	299	274
6	4	44	50
7	4	182	166
8	4	-26	-0
-9	5	-79	-68
-7	5	-196	-184
-6	5	91	70
-5	5	-221	-193
-4	5	53	37
-3	5	80	87
-2	5	58	61
-1	5	479	450
0	5	112	121
1	5	244	199
2	5	229	200
4	5	-28	-21
6	5	-160	-144
7	5	131	132
8	5	-52	-54
-8	6	-38	-12
-7	6	91	74
-6	6	101	86
-5	6	69	64
-4	6	73	39
-3	6	161	111
-2	6	-130	-133
-1	6	313	294
0	6	-128	-106
1	6	215	219
2	6	117	113
3	6	-26	-18
4	6	207	182
5	6	-135	-121
6	6	27	10
7	6	-127	-117
8	6	-150	-136
-8	7	-73	-59
-7	7	123	106
-6	7	80	70
-5	7	65	61
-4	7	269	237
-3	7	-23	-7
-2	7	238	214
0	7	-85	-91
1	7	-59	-65
2	7	-188	-167
3	7	-202	-183
4	7	24	20
5	7	-191	-183
6	7	67	57
7	7	-54	-46
-8	8	54	42
-6	8	-13	-2
-5	8	-77	-76
-4	8	109	96
-3	8	-229	-216
-2	8	88	89
-1	8	-112	-87
0	8	-109	-75
1	8	123	116
2	8	-294	-269
3	8	49	46
4	8	-185	-174
5	8	-79	-74
6	8	-61	-46
7	8	-35	-36
-7	9	98	75
-6	9	-86	-80
-5	9	80	76
-4	9	-168	-141
-3	9	-133	-118
-2	9	-126	-123
-1	9	-197	-182
0	9	-110	-93
2	9	-183	-162
3	9	153	143
4	9	43	41
5	9	33	37
6	9	111	121
7	9	-59	-58
-7	10	-34	-37
-6	10	-131	-113
-5	10	16	14
-4	10	-108	-89
-3	10	12	6
-2	10	97	103
-1	10	-189	-170
0	10	186	171
1	10	-125	-122
2	10	90	94
3	10	52	45
5	10	97	92
6	10	60	58
7	10	67	64
-7	11	-123	-115
-5	11	-48	-47
-4	11	-53	-50
-3	11	66	47
0	11	210	184
1	11	78	72
2	11	107	116
3	11	144	134
4	11	-54	-57
5	11	84	94
6	11	-109	-110
-6	12	90	79
-5	12	104	83
-3	12	220	197
-2	12	-102	-92
-1	12	155	128
1	12	-35	-35
2	12	100	94
4	12	53	50
-5	13	-13	-4
-4	13	101	95
-2	13	31	22
-1	13	48	45
1	13	-86	-84
3	13	-205	-197
5	13	-97	-80
-5	14	-102	-94
-4	14	47	44
-3	14	-107	-96
-2	14	-60	-46
-1	14	33	19
0	14	-113	-106
1	14	65	48
2	14	-63	-56
4	14	-22	-19
-3	15	-66	-61
-2	15	-81	-66
-1	15	-34	-26
0	15	-148	-125
1	15	18	20
2	15	-78	-68
3	15	-11	-4
-2	16	89	81
-1	16	-40	-44
0	16	80	57
L = 2			
-8	0	151	153
-6	0	193	190
-4	0	100	41
4	0	-107	-107
6	0	-222	-203
8	0	-154	-150
-8	1	65	65
-7	1	53	44
-6	1	105	112
-5	1	130	125
-3	1	201	209
-2	1	-214	-224
2	1	-190	-155
3	1	-146	-130
4	1	47	50
5	1	-67	-61
6	1	90	79
8	1	18	14
-9	2	96	96
-8	2	-38	-46
-6	2	-107	-101
-5	2	-117	-131
-4	2	-79	-70
-3	2	-102	-84
-2	2	-89	-77
1	2	-103	-90
2	2	-161	-151
3	2	-149	-172
4	2	91	85
5	2	-150	-145
6	2	77	86
8	2	45	42
-8	3	39	23
-6	3	34	24
-5	3	-255	-236
-3	3	-265	-276
-2	3	-100	-121
-1	3	-110	-117
0	3	-79	-116
1	3	134	161
2	3	59	62
3	3	267	272
4	3	55	46
5	3	145	129
6	3	62	56
7	3	18	21
-9	4	-80	-94
-8	4	-104	-105
-7	4	-54	-50
-6	4	-91	-91
-5	4	70	73
-4	4	42	23
-3	4	60	62
-2	4	79	97
-1	4	88	95
1	4	234	223
2	4	-60	-74
3	4	144	135
5	4	109	102
6	4	122	132
7	4	-58	-61
8	4	104	108
-9	5	22	35
-8	5	-78	-64
-7	5	44	42
-6	5	-115	-102
-5	5	79	68
-4	5	46	26
-3	5	70	26
-2	5	239	244
-1	5	193	182
0	5	234	280
1	5	-94	-55
2	5	132	117
4	5	-57	-65
5	5	-25	-27
6	5	-61	-61
7	5	-98	-94
-8	6	143	138
-7	6	68	65
-6	6	181	175
-5	6	84	99
-4	6	113	99
-3	6	27	7
-2	6	-21	-3
0	6	93	79
1	6	-102	-101
4	6	-143	-138
5	6	114	117
6	6	-146	-157
7	6	33	25
8	6	-86	-77
-8	7	51	39
-5	7	114	108
-3	7	185	187
-2	7	-197	-163
-1	7	44	41
0	7	-142	-128
1	7	-162	-170
2	7	-89	-98
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-1	3	64	77
0	3	-14	-11
1	3	105	110
2	3	-31	-18
3	3	90	88
-7	4	69	92
-5	4	102	103
-4	4	50	49
-3	4	76	73
-2	4	90	80
-1	4	-14	-17
0	4	38	39
1	4	-41	-37
2	4	-21	-13
-6	5	37	39
-5	5	-7	-9
-4	5	40	36
-3	5	-31	-24
-2	5	72	79
-1	5	-71	-69
0	5	58	50
1	5	-28	-29
2	5	-46	-19
-6	6	31	28
-5	6	46	33
-4	6	-83	-81
-2	6	-93	-94
-1	6	-34	-20
0	6	-71	-64
1	6	-46	-32
2	6	-31	-34
-6	7	-60	-49
-4	7	-79	-59
-3	7	17	16
-2	7	-61	-47
-1	7	-32	-19
1	7	-76	-72
-5	8	-144	-128
-3	8	-66	-59
-1	8	37	22
-4	9	33	30
-3	9	39	23
-2	9	-38	-37
-1	9	104	91
0	9	-63	-49
L = 13			
-5	0	-93	-76
-3	0	-182	-167
-1	0	-103	-97
1	0	-41	-36
-6	1	-68	-55
-5	1	23	18
-4	1	-17	-9
-2	1	-15	-15
-1	1	26	4
0	1	-30	-40
1	1	41	38
2	1	-40	-20
-6	2	-128	-124
-5	2	44	38
-4	2	-81	-70
-3	2	65	58
-2	2	35	33
-1	2	50	48
0	2	89	92
1	2	15	9
2	2	87	77
-6	3	96	85
-5	3	29	22
-4	3	63	63
-2	3	53	46
-1	3	-54	-37
0	3	69	44
1	3	-11	-2
-6	4	83	73
-5	4	67	50
-4	4	56	57
-3	4	114	107
-2	4	-35	-39
-1	4	79	75
0	4	-64	-64
-6	5	-37	-32
-5	5	-22	-12
-4	5	-80	-83
-3	5	-36	-25
-2	5	-38	-37
-1	5	23	8
0	5	-21	-15
1	5	-21	-23
-5	6	-40	-37
-4	6	51	37
-3	6	-124	-103
-1	6	-112	-103
0	6	-40	-34
-4	7	-58	-29
-1	7	45	33
0	7	-70	-23
-3	8	-21	-10
L = 14			
-4	0	-87	-74
-2	0	-139	-146
0	0	-37	-19
-5	1	-107	-91
-4	1	112	105
-2	1	80	87
-1	1	36	24
0	1	23	27
-5	2	-80	-61
-4	2	41	35
-3	2	-36	-26
-2	2	39	39
-1	2	91	99
0	2	38	19
-5	3	149	135
-4	3	75	70
-3	3	37	33
-1	3	-44	-43
0	3	-40	-43
-4	4	46	40
-3	4	-29	-28
-2	4	129	112
-1	4	-59	-55
-4	5	-114	-104
-3	5	-72	-67

discontinued since each of the suggested shifts was then less than one-tenth of the appropriate standard deviation. A final difference Fourier showed no unexpected features, thus confirming the correctness of the structure. No indication of the hydrogen atom position was obtained.

Throughout the analysis, the scattering factors for neutral rhenium, manganese, oxygen, and carbon (as compiled by Ibers[26]) were used. The scattering factors of rhenium and manganese were adjusted for the real part of the dispersion correction[27] ($\Delta f'_{Re} = -1.2$, $\Delta f'_{Mn} = +0.4$ electrons), but not for the imaginary components ($\Delta f''_{Re} = 8.3$, $\Delta f''_{Mn} = 0.9$ electrons).

Observed and calculated structure factors are shown in Table I; final atomic parameters are collected in Table II.

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(26) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England. Values for rhenium and manganese are taken from pp 211, 212; those for oxygen and carbon are from pp 202, 203.

(27) See ref 25, pp 215, 216.

TABLE II

FINAL ATOMIC PARAMETERS[a] FOR $HRe_2Mn(CO)_{14}$

Atom	x	y	z	B, A²
Re_1	0.04500 (12)	0.16536 (7)	0.12477 (8)	b
Re_2	−0.10338 (14)	0.36272 (9)	0.09899 (9)	b
Mn	−0.12807 (32)	0.38422 (18)	0.29840 (21)	b
C_1	0.1175 (30)	0.0577 (18)	0.1113 (18)	2.96 (65)
C_2	0.0566 (44)	0.1468 (25)	0.2672 (27)	5.11 (89)
C_3	0.2536 (32)	0.2200 (18)	0.1649 (19)	2.96 (65)
C_4	0.0266 (35)	0.1890 (22)	−0.0150 (23)	4.24 (85)
C_5	−0.1603 (33)	0.1284 (17)	0.0827 (20)	2.84 (63)
C_6	0.1004 (33)	0.4123 (19)	0.1435 (20)	3.37 (69)
C_7	−0.1014 (36)	0.3604 (19)	−0.0270 (22)	3.72 (72)
C_8	−0.3062 (38)	0.3170 (22)	0.0651 (23)	4.32 (78)
C_9	−0.1943 (33)	0.4732 (20)	0.0731 (20)	3.50 (68)
C_{10}	0.0657 (35)	0.3386 (19)	0.3344 (20)	3.55 (76)
C_{11}	−0.0480 (29)	0.4914 (17)	0.2889 (18)	2.82 (62)
C_{12}	−0.3127 (44)	0.4242 (24)	0.2462 (25)	5.01 (90)
C_{13}	−0.2060 (36)	0.2807 (21)	0.2843 (22)	3.96 (73)
C_{14}	−0.1374 (30)	0.3949 (17)	0.4210 (19)	2.80 (85)
O_1	0.1648 (32)	−0.0157 (18)	0.1038 (18)	5.98 (68)
O_2	0.0680 (38)	0.1230 (21)	0.3419 (23)	7.18 (98)
O_3	0.3660 (32)	0.2439 (19)	0.1839 (20)	6.32 (74)
O_4	0.0316 (33)	0.1866 (19)	−0.0903 (20)	6.41 (77)
O_5	−0.2853 (30)	0.0995 (18)	0.0648 (19)	5.76 (64)
O_6	0.2096 (32)	0.4452 (18)	0.1701 (19)	5.91 (71)
O_7	−0.0985 (33)	0.3582 (18)	−0.1121 (19)	5.98 (77)
O_8	−0.4231 (35)	0.2870 (20)	0.0425 (21)	6.86 (78)
O_9	−0.2386 (33)	0.5385 (18)	0.0619 (19)	6.14 (74)
O_{10}	0.1804 (27)	0.3089 (16)	0.3577 (15)	4.76 (59)
O_{11}	0.0072 (32)	0.5595 (19)	0.2800 (19)	6.04 (72)
O_{12}	−0.4284 (37)	0.4562 (20)	0.2188 (22)	7.00 (90)
O_{13}	−0.2490 (33)	0.2112 (20)	0.2689 (20)	6.99 (88)
O_{14}	−0.1490 (30)	0.4005 (17)	0.4964 (18)	5.56 (65)

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Re_1	766 (20)	294 (6)	437 (9)	19 (6)	245 (9)	−7 (4)
Re_2	986 (22)	367 (7)	542 (10)	3 (7)	284 (10)	−1 (5)
Mn[c]	184 (41)	117 (14)	158 (17)	2 (16)	165 (21)	−27 (10)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit of the preceding number. [b] See anisotropic parameters at foot of table. [c] The very low thermal parameters for the manganese atom are rather disturbing. There are two possible explanations: (i) that the $Mn(CO)_5$ group is held rigid by its interaction with the $Re(CO)_5$ group—unlikely because of the normal thermal parameters of oxygen and carbon atoms; (ii) that the crystal is doped with a small percentage of $HRe_3(CO)_{14}$. This is very possible,[20,31] but the amount of $HRe_3(CO)_{14}$ must be small, or we would have (a) a different observed density, (b) more distinct "Mn–Mn" peaks on the Patterson, (c) an "Mn–Re_2" bond length close to 3.02 A, and (d) a large peak on the final difference Fourier. None of these features is observed.

TABLE III

BOND LENGTHS AND IMPORTANT INTRAMOLECULAR CONTACTS[a] IN $HRe_2Mn(CO)_{14}$

Atoms	Distance, A	Atoms	Distance, A
(a) Bond Lengths			
$Re_1\cdots Re_2$	3.392 ± 0.002	Re_2–Mn	2.960 ± 0.003
$Re_1\cdots Mn$	4.806 ± 0.003		
Re_1–C_1	1.86 ± 0.03	C_1–O_1	1.26 ± 0.04
Re_1–C_2	2.04 ± 0.04	C_2–O_2	1.12 ± 0.05
Re_1–C_3	2.05 ± 0.03	C_3–O_3	1.07 ± 0.04
Re_1–C_4	2.00 ± 0.03	C_4–O_4	1.10 ± 0.04
Re_1–C_5	1.93 ± 0.03	C_5–O_5	1.21 ± 0.04
Re_2–C_6	1.99 ± 0.03	C_6–O_6	1.11 ± 0.04
Re_2–C_7	1.82 ± 0.03	C_7–O_7	1.23 ± 0.04
Re_2–C_8	1.95 ± 0.03	C_8–O_8	1.15 ± 0.05
Re_2–C_9	1.93 ± 0.03	C_9–O_9	1.11 ± 0.04
Re–C (av)	1.953		
Mn–C_{10}	1.88 ± 0.03	C_{10}–O_{10}	1.13 ± 0.04
Mn–C_{11}	1.87 ± 0.03	C_{11}–O_{11}	1.22 ± 0.04
Mn–C_{12}	1.79 ± 0.04	C_{12}–O_{12}	1.15 ± 0.05
Mn–C_{13}	1.78 ± 0.03	C_{13}–O_{13}	1.17 ± 0.04
Mn–C_{14}	1.80 ± 0.03	C_{14}–O_{14}	1.12 ± 0.04
Mn–C (av)	1.823	C–O (av)	1.153
(b) Metal–Oxygen Distances			
$Re_1\cdots O_1$	3.12 ± 0.03	$Re_2\cdots O_6$	3.09 ± 0.03
$Re_1\cdots O_2$	3.14 ± 0.03	$Re_2\cdots O_7$	3.05 ± 0.03
$Re_1\cdots O_3$	3.13 ± 0.03	$Re_2\cdots O_8$	3.10 ± 0.03
$Re_1\cdots O_4$	3.03 ± 0.03	$Re_2\cdots O_9$	3.04 ± 0.03
$Re_1\cdots O_5$	3.13 ± 0.03	$Re\cdots O$ (av)	3.097
$Mn\cdots O_{10}$	3.00 ± 0.02	$Mn\cdots O_{13}$	2.94 ± 0.03
$Mn\cdots O_{11}$	3.09 ± 0.03	$Mn\cdots O_{14}$	2.92 ± 0.03
$Mn\cdots O_{12}$	2.94 ± 0.03	$Mn\cdots O$ (av) = 2.978	
(c) Contacts between Staggered Carbonyl Groups			
$C_6\cdots C_{10}$	3.08 ± 0.04	$O_6\cdots O_{10}$	3.52 ± 0.04
$C_6\cdots C_{11}$	3.08 ± 0.04	$O_6\cdots O_{11}$	3.32 ± 0.04
$C_9\cdots C_{11}$	3.03 ± 0.04	$O_9\cdots O_{11}$	3.34 ± 0.04
$C_9\cdots C_{12}$	3.09 ± 0.05	$O_9\cdots O_{12}$	3.49 ± 0.04
$C_8\cdots C_{12}$	3.12 ± 0.05	$O_8\cdots O_{12}$	3.70 ± 0.05
$C_8\cdots C_{13}$	3.08 ± 0.05	$O_8\cdots O_{13}$	3.42 ± 0.04
(d) Contacts between Eclipsed Carbonyl Groups			
$C_3\cdots C_6$	3.34 ± 0.04	$O_3\cdots O_6$	3.48 ± 0.04
$C_4\cdots C_7$	2.95 ± 0.05	$O_4\cdots O_7$	2.95 ± 0.04
$C_5\cdots C_8$	3.26 ± 0.04	$O_5\cdots O_8$	3.21 ± 0.04
(e) Other Contacts			
$O_2\cdots O_{10}$	3.11 ± 0.04	$O_3\cdots O_{10}$	3.57 ± 0.04
$O_2\cdots O_{13}$	3.16 ± 0.04	$O_5\cdots O_{13}$	3.36 ± 0.04

[a] Estimated standard deviations do not include any contributions from possible errors in unit-cell dimensions (which may be as much as 1 part in 700). This will have a significant effect only for errors in metal–metal distances.

The Molecular Structure

Table III lists the important bond lengths and contacts within the molecule; bond angles are shown in Table IV. The stereochemistry of the molecule and the numbering scheme for the atoms are shown in Figure 1.

The three metal atoms are arranged in a *cis* configuration. In the crystal lattice the molecule has approximate C_s symmetry, with the mirror plane ($0.8759X + 0.3904Y + 0.2832Z = 1.4313$[28]) containing the three metal atoms and six carbonyl groups (see Table V). The Mn–Re_2 distance of 2.960 ± 0.003 A is in good agreement with the value of ~2.97 A which might be predicted from the known metal–metal distances of ~3.02 A in $Re_2(CO)_{10}$,[29] 2.923 A in $Mn_2(CO)_{10}$,[30] and 2.914 A in $[(C_2H_5)_3PMn(CO)_4]_2$.[31] The $Re_1\cdots Re_2$ distance of 3.392 ± 0.002 A is ~0.37 A longer than a simple rhenium–rhenium bond and it is proposed that the hydrogen atom known[32] to be present in the molecule is located *somewhere* (*vide infra*) between these two rhenium atoms. [The $Re_1\cdots Mn$ distance of 4.806 ± 0.003 A is obviously too long to be considered seriously as a location for a bridging hydrogen atom; similarly, the regular stereochemistry around each metal atom would seem to preclude the possibility of the hydrogen atom being associated specifically with any *one* metal atom, since it is now conclusively established that the hydride ligand must occupy a distinct coordination position.]

Whereas one would predict an angle of 90° for the *cis* configuration of the metal skeleton, the observed value for the angle $Re_1\cdots Re_2$—Mn is 98.09 ± 0.07°; furthermore, the vertical coordination planes of Re_1 and Re_2 (b and e of Table VI) make an angle of 16.2° in

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[28] All planes are given in orthogonal coordinates for the convenience of the reader. The transformations are $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$.

[29] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

[30] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

[31] M. J. Bennett, Ph.D. Thesis, Sheffield, England, 1965.

[32] J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 1759 (1967).

TABLE IV

INTERATOMIC ANGLES IN $HRe_2Mn(CO)_{14}$

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles between Metal Atoms			
$Re_1\cdots Re_2–Mn$	98.09 ± 0.07	$Re_1\cdots Mn\cdots Re_2$	44.33 ± 0.05
$Re_2\cdots Re_1\cdots Mn$	37.58 ± 0.04		
(b) M–C–O Angles			
$Re_1–C_1–O_1$	178.5 ± 2.5	$Re_2–C_8–O_8$	176.5 ± 3.2
$Re_1–C_2–O_2$	168.2 ± 3.6	$Re_2–C_9–O_9$	175.7 ± 2.9
$Re_1–C_3–O_3$	175.3 ± 2.8	$Mn–C_{10}–O_{10}$	177.6 ± 2.8
$Re_1–C_4–O_4$	165.5 ± 3.1	$Mn–C_{11}–O_{11}$	177.1 ± 2.5
$Re_1–C_5–O_5$	173.0 ± 2.6	$Mn–C_{12}–O_{12}$	173.5 ± 3.5
$Re_2–C_6–O_6$	174.8 ± 2.8	$Mn–C_{13}–O_{13}$	173.4 ± 3.0
$Re_2–C_7–O_7$	179.2 ± 2.8	$Mn–C_{14}–O_{14}$	177.2 ± 2.7
(c) Angles at the Metal Atoms			
$C_1–Re_1–C_2$	93.2 ± 1.4	$O_1\cdots Re_1\cdots O_2$	88.5 ± 0.8
$C_1–Re_1–C_3$	94.1 ± 1.2	$O_1\cdots Re_1\cdots O_3$	92.9 ± 0.7
$C_1–Re_1–C_4$	89.9 ± 1.3	$O_1\cdots Re_1\cdots O_4$	85.3 ± 0.8
$C_1–Re_1–C_5$	92.7 ± 1.2	$O_1\cdots Re_1\cdots O_5$	91.0 ± 0.7
$C_2–Re_1–C_3$	90.0 ± 1.4	$O_2\cdots Re_1\cdots O_3$	91.3 ± 0.8
$C_2–Re_1–C_4$	176.9 ± 1.5	$O_2\cdots Re_1\cdots O_4$	173.8 ± 0.8
$C_2–Re_1–C_5$	92.1 ± 1.4	$O_2\cdots Re_1\cdots O_5$	89.3 ± 0.8
$C_3–Re_1–C_4$	90.6 ± 1.2	$O_3\cdots Re_1\cdots O_4$	89.6 ± 0.8
$C_3–Re_1–C_5$	172.7 ± 1.2	$O_3\cdots Re_1\cdots O_5$	176.0 ± 0.7
$C_4–Re_1–C_5$	86.9 ± 1.3	$O_4\cdots Re_1\cdots O_5$	90.1 ± 0.8
$Re_2\cdots Re_1–C_1$	168.2 ± 0.9	$Re_2\cdots Re_1\cdots O_1$	168.7 ± 0.5
$Re_2\cdots Re_1–C_2$	98.4 ± 1.1	$Re_2\cdots Re_1\cdots O_2$	102.5 ± 0.6
$Re_2\cdots Re_1–C_3$	88.1 ± 0.8	$Re_2\cdots Re_1\cdots O_3$	89.6 ± 0.5
$Re_2\cdots Re_1–C_4$	78.6 ± 1.0	$Re_2\cdots Re_1\cdots O_4$	83.7 ± 0.6
$Re_2\cdots Re_1–C_5$	84.7 ± 0.9	$Re_2\cdots Re_1\cdots O_5$	86.4 ± 0.5
$Re_1\cdots Re_2–C_6$	90.4 ± 0.9	$Re_1\cdots Re_2\cdots O_6$	92.1 ± 0.5
$Re_1\cdots Re_2–C_7$	88.4 ± 1.0	$Re_1\cdots Re_2\cdots O_7$	88.1 ± 0.5
$Re_1\cdots Re_2–C_8$	91.3 ± 1.0	$Re_1\cdots Re_2\cdots O_8$	90.3 ± 0.6
$Re_1\cdots Re_2–C_9$	175.3 ± 0.9	$Re_1\cdots Re_2\cdots O_9$	176.3 ± 0.5
$C_6–Re_2–C_7$	92.9 ± 1.3	$O_6\cdots Re_2\cdots O_7$	93.5 ± 0.8
$C_6–Re_2–C_8$	175.3 ± 1.3	$O_6\cdots Re_2\cdots O_8$	175.2 ± 0.8
$C_6–Re_2–C_9$	91.8 ± 1.2	$O_6\cdots Re_2\cdots O_9$	88.6 ± 0.8
$C_7–Re_2–C_8$	91.5 ± 1.4	$O_7\cdots Re_2\cdots O_8$	90.8 ± 0.8
$C_7–Re_2–C_9$	87.3 ± 1.3	$O_7\cdots Re_2\cdots O_9$	88.2 ± 0.8
$C_8–Re_2–C_9$	86.9 ± 1.3	$O_8\cdots Re_2\cdots O_9$	89.3 ± 0.8
$Mn–Re_2–C_6$	88.4 ± 0.9	$Mn–Re_2\cdots O_6$	87.4 ± 0.5
$Mn–Re_2–C_7$	173.4 ± 1.0	$Mn–Re_2\cdots O_7$	173.7 ± 0.6
$Mn–Re_2–C_8$	87.1 ± 1.0	$Mn–Re_2\cdots O_8$	88.1 ± 0.6
$Mn–Re_2–C_9$	86.1 ± 0.9	$Mn–Re_2\cdots O_9$	85.6 ± 0.6
$Re_2–Mn–C_{10}$	83.8 ± 0.9	$Re_2–Mn\cdots O_{10}$	84.2 ± 0.5
$Re_2–Mn–C_{11}$	83.8 ± 0.8	$Re_2–Mn\cdots O_{11}$	82.9 ± 0.5
$Re_2–Mn–C_{12}$	87.9 ± 1.2	$Re_2–Mn\cdots O_{12}$	89.6 ± 0.6
$Re_2–Mn–C_{13}$	85.7 ± 1.0	$Re_2–Mn\cdots O_{13}$	83.4 ± 0.6
$Re_2–Mn–C_{14}$	178.0 ± 0.9	$Re_2–Mn\cdots O_{14}$	178.4 ± 0.5
$C_{10}–Mn–C_{11}$	89.8 ± 1.2	$O_{10}\cdots Mn\cdots O_{11}$	90.0 ± 0.7
$C_{10}–Mn–C_{12}$	171.6 ± 1.5	$O_{10}\cdots Mn\cdots O_{12}$	173.3 ± 0.8
$C_{10}–Mn–C_{13}$	90.4 ± 1.4	$O_{10}\cdots Mn\cdots O_{13}$	88.2 ± 0.7
$C_{10}–Mn–C_{14}$	94.3 ± 1.3	$O_{10}\cdots Mn\cdots O_{14}$	94.6 ± 0.7
$C_{11}–Mn–C_{12}$	90.2 ± 1.5	$O_{11}\cdots Mn\cdots O_{12}$	89.1 ± 0.8
$C_{11}–Mn–C_{13}$	169.4 ± 1.3	$O_{11}\cdots Mn\cdots O_{13}$	166.2 ± 0.8
$C_{11}–Mn–C_{14}$	96.7 ± 1.2	$O_{11}\cdots Mn\cdots O_{14}$	98.4 ± 0.8
$C_{12}–Mn–C_{13}$	88.0 ± 1.6	$O_{12}\cdots Mn\cdots O_{13}$	91.2 ± 0.9
$C_{12}–Mn–C_{14}$	94.0 ± 1.5	$O_{12}\cdots Mn\cdots O_{14}$	91.5 ± 0.8
$C_{13}–Mn–C_{14}$	93.8 ± 1.4	$O_{13}\cdots Mn\cdots O_{14}$	95.4 ± 0.8

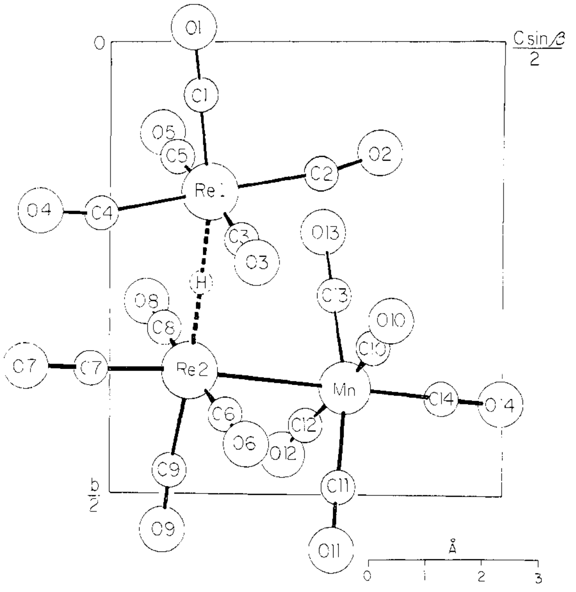

Figure 1.—$HRe_2Mn(CO)_{14}$ viewed along *a*.

TABLE V

DISTANCES FROM THE PLANE[a] OF THE METAL ATOMS IN $HRe_2Mn(CO)_{14}$

Plane:[28] $0.8759X + 0.3904Y + 0.2832Z = 1.4313$

Atom	Distance, A	Atom	Distance, A
Re_1	0.000	Mn	0.000
Re_2	0.000		
O_1	−0.15 ± 0.03	C_1	−0.08 + 0.03
O_2	+0.00 ± 0.03	C_2	+0.03 ± 0.04
O_4	−0.05 ± 0.03	C_4	−0.05 ± 0.03
O_7	−0.06 ± 0.03	C_7	−0.04 ± 0.03
O_9	−0.03 ± 0.03	C_9	−0.07 ± 0.03
O_{14}	−0.00 ± 0.03	C_{14}	+0.03 ± 0.03
O_3	+3.12 ± 0.03	O_5	−3.12 ± 0.03
C_3	+2.05 ± 0.03	C_5	−1.92 ± 0.03
O_6	+3.09 ± 0.03	O_8	−3.09 ± 0.03
C_6	+1.98 ± 0.03	C_8	−1.95 ± 0.03
O_{10}	+2.07 ± 0.02	O_{12}	−2.03 ± 0.03
C_{10}	+1.31 ± 0.03	C_{12}	−1.28 ± 0.04
O_{11}	+2.18 ± 0.03	O_{13}	−2.07 ± 0.03
C_{11}	+1.31 ± 0.03	C_{13}	−1.28 ± 0.03

[a] Metal atoms each have unit weight; all other atoms have zero weight.

the pseudo mirror plane of the molecule, resulting in a large difference in the angles $Re_2\cdots Re_1\cdots O_2$ (102.5 ± 0.6°) and $Re_2\cdots Re_1\cdots O_4$ (83.7 ± 0.6°). There appears to be no obvious electronic interpretation of this distortion from the regular octahedral value, and the observed intramolecular geometry is consistent with the intramolecular contacts $O_2\cdots O_{10}$ (3.11 ± 0.04 A) and $O_2\cdots O_{13}$ (3.16 ± 0.04 A) dominating the over-all conformation of the molecule. Surprisingly, the closest intramolecular contact ($O_4\cdots O_7$ = 2.95 ± 0.04 A) and the most important *intermolecular* interactions (*vide infra*) act in such a way as to *decrease* the $Re_1\cdots Re_2$–Mn angle.

The carbonyl ligands in the $(OC)_4Re–Mn(CO)_5$ portion of the molecule are in a strictly staggered conformation. The two sets of radial carbonyl groups are displaced slightly from a regular octahedral arrangement, such that the carbonyl ligands bend toward each other [$\angle(Re_2–Mn–C_{\text{radial}}) = 85.2°$ (av); $\angle(Re_2–Mn\cdots O_{\text{radial}}) = 85.0°$ (av); $\angle(Mn–Re_2–C_{\text{radial}}) = 87.2°$ (av); $\angle(Mn–Re_2\cdots O_{\text{radial}}) = 87.0°$ (av)]. Similar distortions have been observed for $Mn_2(CO)_{10}$,[30] $Tc_2(CO)_{10}$,[33] and $HMn(CO)_5$[9] and are probably general for $M(CO)_5X$ species ($X \neq CO$).[34]

The carbonyl groups in the $(OC)_4Re–(H)–Re(CO)_5$ portion of the molecule are in an eclipsed configuration (as is the case in the $[HCr_2(CO)_{10}]^-$ ion[18]). Any possible distortion of these carbonyl groups away from or toward each other is masked by the severe angular effects resulting from the $Re_1\cdots Re_2$–Mn angle of 98.1°

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(33) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).

(34) See, for example, R. M. Wing, and D. C. Crocker, *ibid.*, **6**, 289 (1967); and P. S. Braterman, R. Bau, and H. D. Kaesz, *ibid.*, **6**, 2097 (1967).

TABLE VI

DIRECTION COSINES FOR LEAST-SQUARES PLANES[28] IN THE $HRe_2Mn(CO)_{14}$ MOLECULE[a]

Plane	Atoms	c_1	c_2	c_3	d
a	Re_1, C_1, O_1, C_2, O_2, C_4, O_4	0.8953	0.3545	0.2693	1.3000
b	Re_1, C_1, O_1, C_3, O_3, C_5, O_5	−0.2161	−0.1800	0.9596	1.1767
c	Re_1, C_2, O_2, C_3, O_3, C_4, O_4, C_5, O_5	−0.3956	0.9161	0.0637	2.5669
d	Re_2, C_6, O_6, C_7, O_7, C_8, O_8	0.3704	−0.9167	0.1496	−5.5946
e	Re_2, C_6, O_6, C_8, O_8, C_9, O_9	−0.3364	0.0726	0.9388	2.2337
f	Re_2, C_7, O_7, C_9, O_9	0.8764	0.4012	0.2660	1.4579
g	Mn, C_{10}, O_{10}, C_{11}, O_{11}, C_{12}, O_{12}, C_{13}, O_{13}	−0.3080	0.1087	0.9451	5.1098
h	Mn, C_{10}, O_{10}, C_{12}, O_{12}, C_{14}, O_{14}	0.3926	0.9182	0.0511	4.8421
i	Mn, C_{11}, O_{11}, C_{13}, O_{13}, C_{14}, O_{14}	0.8588	−0.3763	0.3475	−2.9210

[a] The equation for each plane is in the form $c_1X + c_2Y + c_3Z = d$.

TABLE VII

A SUMMARY OF STRUCTURAL STUDIES ON TRANSITION METAL HYDRIDES

Species	Technique	Bond	Length, A	Ref	Comment
Mn–H	High-resolution visible + ultraviolet spectroscopy	Mn–H	1.731	a	
Ni–H		Ni–H	1.475	a	
Co–H		Co–H	1.542; 1.593	a	Different states
$HMn(CO)_5$	X-Ray	Mn–H	(∼1.5–1.6)	9	Estimated
$HMn(CO)_5$	Nmr	Mn–H	1.28 ± 0.01	13	In dispute[f]
$H_2Fe(CO)_4$	Nmr	Fe–H	1.1–1.5	12	Depends on ∠(H–Fe–H)[b]
$HCo(CO)_4$	Nmr	Co–H	1.2 ± 0.1	14	In dispute[f]
$HPtBr(P(C_2H_5)_3)_2$	X-Ray	Pt–H	...	3	
$HPtCl(P(C_6H_5)_2C_2H_5)_2$	X-Ray	Pt–H	...	10	
$HOsBr(CO)(P(C_6H_5)_3)_3$	X-Ray	Os–H	...	4	
$HRh(CO)(P(C_6H_5)_3)_3$	X-Ray	Rh–H	1.60 ± 0.12	5	
$(\pi\text{-}C_5H_5)_2MoH_2$	X-Ray	Mo–H	1.2 ± 0.3	6	Has been disputed[d]
K_2TcH_9	X-Ray	Tc–H	...	7	
K_2ReH_9	X-Ray	Re–H	...	8	
K_2ReH_9	Neutron	Re–H	1.68 ± 0.01	11	
$[C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}\{H\}$	X-Ray	Mo–H	(∼1.8)	16	Estimated
$[HFe_3(CO)_{11}]^-$	X-Ray	Fe–H		17	
$HMn_3(CO)_{10}(BH_3)_2$	X-Ray	Mn–H	1.65 ± 0.1	15	
$[HCr_2(CO)_{10}]^-$	X-Ray	Cr–H	1.705	18	Assuming linear, symmetric M–H–M
$HRe_2Mn(CO)_{14}$	X-Ray	Re–H	1.696	e	

[a] G. Herzberg "Molecular Spectra and Molecular Structure. Infrared Spectra of Diatomic Molecules," 2nd ed, D. van Nostrand Co., New York, N. Y. [b] Originally assumed to be ∼120°,[12] which gives Fe–H = 1.1 A, but now thought[c] to be closer to 90°, whence Fe–H = ∼1.5 A after correction is made for the suspected[9] intermolecular H···H contacts. [c] A. P. Ginsberg, "Transition Metal Chemistry," Vol. 1, Marcel Dekker Inc., New York, N. Y., 1965, pp 208, 209. [d] S. C. Abrahams and A. P. Ginsberg, *Inorg. Chem.*, **5**, 500 (1966). [e] This work. [f] NOTE ADDED IN PROOF.—Recent calculations (which include quadrupole effects) suggest the revised values: Mn–H = 1.44 ± 0.03 A, Co–H = 1.59 ± 0.04 A [G. M. Sheldrick, *Chem. Commun.*, 751 (1967)].

and intramolecular overcrowding between the $Re(CO)_5$ and $Mn(CO)_5$ moieties.

Average bond distances in the $HRe_2Mn(CO)_{14}$ molecule are shown in Table III. The presence of two rhenium atoms in the molecule results in rather large esd's for bond lengths involving carbon and oxygen atoms and does not permit any comment on individual bond lengths involving light atoms. However, the *average* bond lengths are in good agreement with other measurements; the average Mn–C distance of 1.823 A agrees exactly with the average value (1.823 A) reported for $Mn_2(CO)_{10}$.[30] The esd's in the present molecule are sufficiently large that it is impossible to determine with certainty whether the axial metal–carbon bonds in the $M(CO)_5$ groups are longer than the radial metal–carbon bonds. Such a phenomenon has been claimed to occur both in $Mn_2(CO)_{10}$ and in $Tc_2(CO)_{10}$, as a result of the greater π character in the axial metal–carbon linkages.[33]

The Metal–Hydrogen Linkage

The regular stereochemistry around each of the metal ions and the long $Re_1 \cdots Re_2$ distance (3.392 ± 0.002 A) lead us to believe that the hydrogen atom is situated between the two rhenium atoms. If we assume a linear, symmetric Re–H–Re bond, then the Re–H distance is 1.696 A, very close to the bond lengths in the chemically rather dissimilar K_2ReH_9 [Re–H = 1.68 ± 0.01 A (av)[11]] and in general agreement with other bridging hydrides (see Table VII). It should be stressed that we have not ascertained (i) whether the Re–H–Re linkage is linear or (ii) whether it is symmetric. In fact, as a result of the steric interaction between the $Re(CO)_5$ and $Mn(CO)_5$ groups it is possible that the hydrogen atom does not occupy a position immediately between the two rhenium atoms but may be displaced slightly to one side of the $Re \cdots Re$ vector, even if the Re–H–Re linkage is symmetric.

Intermolecular Contacts

Table VIII summarizes all intermolecular contacts below 3.3 A. There appears to be no rationale of the $Re_1 \cdots Re_2$–Mn angle in terms of intermolecular contacts. There are only two contacts significantly less than the intramolecular contacts $O_2 \cdots O_{10}$ and $O_2 \cdots O_{13}$. Although each of these intermolecular repulsions involves O_2, the first [$O_2 \cdots O_{12}$ $(-x - 1/2, +y - 1/2, -z + 1/2)$ = 2.96 A] operates in such a way as to push O_2 down toward O_{10} and O_{13}, thus decreasing the angle between the vertical coordination planes of Re_1 and Re_2 and, presumably, decreasing the angle $Re_1 \cdots Re_2$–Mn; the second [$O_2 \cdots O_7$ $(+x + 1/2, -y + 1/2, +z + 1/2)$ = 3.00 A] acts in the x direction, *i.e.*, more

TABLE VIII

INTERMOLECULAR CONTACTS TO 3.3 A FOR $HRe_2Mn(CO)_{14}$

$C_1 \cdots O_{14}$	$(x + 1/2, -y + 1/2, z - 1/2)$	3.15
$C_2 \cdots O_7$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.19
$C_2 \cdots O_{12}$	$(-x - 1/2, +y - 1/2, -z + 1/2)$	3.27
$C_4 \cdots O_{10}$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.22
$C_4 \cdots O_{14}$	$(x + 1/2, -y + 1/2, z - 1/2)$	3.30
$C_5 \cdots O_1$	$(-x, -y, -z)$	3.21
$C_7 \cdots O_2$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.13
$C_8 \cdots O_2$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.23
$O_1 \cdots O_{10}$	$(-x + 1/2, +y - 1/2, -z + 1/2)$	3.10
$O_1 \cdots O_6$	$(-x + 1/2, +y - 1/2, -z + 1/2)$	3.19
$O_1 \cdots O_{14}$	$(x + 1/2, -y + 1/2, z - 1/2)$	3.20
$O_1 \cdots C_5$	$(-x, -y, -z)$	3.21
$O_1 \cdots O_5$	$(-x, -y, -z)$	3.23
$O_1 \cdots O_4$	$(-x, -y, -z)$	3.24
$O_1 \cdots O_{11}$	$(-x + 1/2, +y - 1/2, -z + 1/2)$	3.26
$O_2 \cdots O_{12}$	$(-x - 1/2, +y - 1/2, -z + 1/2)$	2.96
$O_2 \cdots O_7$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.00
$O_2 \cdots C_7$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.13
$O_2 \cdots O_8$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.20
$O_2 \cdots C_8$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.23
$O_3 \cdots O_{11}$	$(-x + 1/2, +y - 1/2, -z + 1/2)$	3.13
$O_3 \cdots O_8$	$(x + 1, y, z)$	3.27
$O_3 \cdots O_7$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.28
$O_4 \cdots O_{10}$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.14
$O_4 \cdots O_{14}$	$(x + 1/2, -y + 1/2, z - 1/2)$	3.19
$O_4 \cdots O_1$	$(-x, -y, -z)$	3.24
$O_5 \cdots O_1$	$(-x, -y, -z)$	3.23
$O_5 \cdots O_{10}$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.25
$O_5 \cdots O_{14}$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.25
$O_5 \cdots O_{14}$	$(-x - 1/2, +y - 1/2, -z + 1/2)$	3.28
$O_6 \cdots O_1$	$(-x + 1/2, y + 1/2, -z + 1/2)$	3.19
$O_6 \cdots O_{12}$	$(x + 1, y, z)$	3.25
$O_7 \cdots O_2$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.00
$O_7 \cdots O_{11}$	$(-x, -y + 1, -z)$	3.07
$O_7 \cdots C_2$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.19
$O_7 \cdots O_3$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.28
$O_8 \cdots O_2$	$(x - 1/2, -y + 1/2, z - 1/2)$	3.20
$O_8 \cdots O_3$	$(x - 1, y, z)$	3.27
$O_{10} \cdots O_1$	$(-x + 1/2, y + 1/2, -z + 1/2)$	3.10
$O_{10} \cdots O_4$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.14
$O_{10} \cdots C_5$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.22
$O_{10} \cdots O_5$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.25
$O_{11} \cdots O_7$	$(-x, -y + 1, -z)$	3.07
$O_{11} \cdots O_3$	$(-x + 1/2, +y + 1/2, -z + 1/2)$	3.13
$O_{11} \cdots O_{14}$	$(-x, -y + 1, -z + 1)$	3.17
$O_{11} \cdots O_1$	$(-x + 1/2, y + 1/2, -z + 1/2)$	3.26
$O_{12} \cdots O_2$	$(-x - 1/2, y + 1/2, -z + 1/2)$	2.96
$O_{12} \cdots O_6$	$(x - 1, y, z)$	3.25
$O_{12} \cdots C_2$	$(-x - 1/2, y + 1/2, -z + 1/2)$	3.27
$O_{14} \cdots C_1$	$(x - 1/2, -y + 1/2, z + 1/2)$	3.15
$O_{14} \cdots O_{11}$	$(-x, -y + 1, -z + 1)$	3.17
$O_{14} \cdots O_4$	$(x - 1/2, -y + 1/2, z + 1/2)$	3.19
$O_{14} \cdots O_1$	$(x - 1/2, -y + 1/2, z + 1/2)$	3.20
$O_{14} \cdots O_5$	$(x + 1/2, -y + 1/2, z + 1/2)$	3.25
$O_{14} \cdots O_5$	$(-x - 1/2, y + 1/2, -z + 1/2)$	3.28
$O_{14} \cdots C_4$	$(x - 1/2, -y + 1/2, z + 1/2)$	3.30

or less in the plane of the equatorial carbonyl groups of the $Re(CO)_5$ group, and should not significantly affect the $Re_1 \cdots Re_2-Mn$ angle.

Acknowledgments.—We are grateful to Professor H. D. Kaesz, who has been extremely helpful in discussions. This research has been generously supported by grants from the National Science Foundation (GP-4225) and the Advanced Research Projects Agency (SD-88).

CONTRIBUTION FROM THE CYANAMID EUROPEAN RESEARCH INSTITUTE,
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The Pentacarbonyls of Ruthenium and Osmium. II. Dihydridotetracarbonylosmium and Its Substitution Reactions

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Received June 26, 1967

Dihydridotetracarbonylosmium, $OsH_2(CO)_4$, has been obtained in high yields by the reaction of osmium tetroxide with carbon monoxide and hydrogen at elevated temperature and pressure and also by allowing pentacarbonylosmium to react with molecular hydrogen. The nuclear magnetic resonance and infrared spectra are in agreement with a *cis*-octahedral structure of symmetry C_{2v} for the dihydridotetracarbonyl. Upon deuteration, a small shift of the carbonyl stretching vibrations is observed, which is explained by removal of the resonance interaction existing in $OsH_2(CO)_4$ between the metal–hydrogen and the carbonyl stretching vibrational states. Substitution reactions of $OsH_2(CO)_4$ are also reported. With triphenylphosphine one carbon monoxide group is substituted with formation of $OsH_2(CO)_3P(C_6H_5)_3$. Infrared and nmr data of the latter compound and the corresponding deuterated species suggest an all-*cis* configuration. Finally the room-temperature reactions of $OsH_2(CO)_4$ with carbon tetrachloride and carbon tetrabromide led to the formation of the *cis*-dihalogeno compounds $OsX_2(CO)_4$ (X = Cl, Br).

In the first paper of this series[1] we reported the infrared spectra of $Ru(CO)_5$ and $Os(CO)_5$ and suggested a trigonal-bipyramidal configuration in solution for both of them. During the synthesis of $Os(CO)_5$ a more volatile fraction than the pentacarbonyl was observed. In the present paper we wish to report that this substance has now been identified as dihydridotetracarbonylosmium, $OsH_2(CO)_4$. This compound was suspected by Hieber and Stallmann[2] to be present

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[1] F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, **6**, 1220 (1967).

[2] W. Hieber and H. Stallmann, *Z. Elektrochem.*, **49**, 288 (1943).