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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · OCTOBER 1966

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Stereochemically Nonrigid Organometallic Compounds. I. π-Cyclopentadienyliron Dicarbonyl σ-Cyclopentadiene[1]

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received March 11, 1966*

Abstract: The problem of the nmr equivalence of the protons of the nonsandwich bonded C_5H_5 group of $(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2C_5H_5$ has been investigated by X-ray crystallography and nuclear resonance spectroscopy at low temperatures. In the crystal, the second C_5H_5 group is present as a normal σ-bonded 2,4-cyclopentadienyl group. The unit cell is monoclinic, space group $P2_1/c$, with dimensions $a = 12.53 \pm 0.03$, $b = 7.50 \pm 0.02$, $c = 11.29 \pm 0.02$ A, and $\beta = 98.0 \pm 0.5°$, and contains four formula units. In solution below about $-60°$ a proton nmr spectrum consisting of three absorption bands at $\tau \sim 4$, 5.6, and 6.5 with relative intensities of 4 : 5 : 1 is observed, the first one having partially resolved structure. This spectrum indicates that in solution the molecular configuration of greatest stability is similar to that in the crystal, which contains a σ-bonded ring. Moreover, from a detailed consideration of the fine structure of the A_2B_2 multiplet of relative intensity four and, particularly, of the unsymmetrical variation in its envelope as a function of temperature, it is concluded that an intramolecular reorientation process occurs by repeated 1,2 shifts, probably passing through a metal–olefin transition state.

The literature presently records several examples of molecules in which all the protons of an unsaturated carbocyclic ring which is bound to a metal atom are nmr equivalent in solution at room temperature despite the fact that elementary valence considerations or the known molecular structure of the crystalline compound would not lead one to expect all of them to be chemically equivalent. Some of these molecules are $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$,[4] $(C_5H_5)_2Hg$,[4,5] $(C_8H_8)Fe(CO)_3$,[6,7] and $(C_7H_7)Fe(CO)_3ClO_4$.[8] The first example of this phenomenon to be discovered appears to have been the $(C_5H_5)_2Hg$ molecule, and, in order to explain the nmr equivalence, Piper and Wilkinson proposed[4] that each ring was σ bonded to the mercury atom, but that the point of attachment changed from one carbon atom to another rapidly enough that the expected separate proton resonance lines were collapsed to a single sharp peak. The same explanation was proposed[4] for $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$. For some years these interesting phenomena and the equally interesting explanation suggested by Piper and Wilkinson remained the only ones of their kind and apparently excited little active curiosity. Considerably later the $(C_8H_8)Fe(CO)_3$ molecule was prepared,[6] and when its unsymmetrical structure in the crystalline state was established a similar explanation was suggested[6] as a possibility. In this instance a rapid shift of a π-orbital-to-metal rather than a σ-orbital-to-metal interaction would be involved. Most recently, the $(C_7H_7)Fe(CO)_3^+$ case has been reported, although here it is perhaps not quite so clear that an inherently unsymmetrical ground configuration must be assumed since few physical data have as yet been reported. However, it seems probable that this case may be qualitatively similar to the others.

Assuming that the general idea suggested by Wilkinson and Piper is correct (even if the details might be a little different), these molecules constitute examples of stereochemically nonrigid structures.[9] This paper[10] is the first in a series of reports describing investigations aimed at establishing more precisely the nature of the dynamic processes involved in the nonrigidity of organometallic compounds.[10a]

Experimental Section

Preparation and Purification. π-Cyclopentadienyliron dicarbonyl σ-cyclopentadiene was prepared using Piper and Wilkinson's method.[4] The crude product, which was separated from $(\pi\text{-}C_5H_5)_2\text{-}Fe_2(CO)_4$ by chromatography on alumina with benzene as the eluent and finally from ferrocene by chromatography with hexane as the eluent, was a waxy solid. A recrystallization from pentane

(1) Research supported by the National Science Foundation under Grants GP 3468 and GP 4329.

(2) NSF Predoctoral Fellow, 1963–1966.

(3) NSF Postdoctoral Fellow, 1965–1966.

(4) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(5) T. S. Piper and G. Wilkinson, *ibid.*, **2**, 32 (1956).

(6) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6240 (1960); M. A. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959); K. Nakamura, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

(7) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

(8) J. E. Mahler, D. A. K. Jones, and R. Pettit, *ibid.*, **86**, 3589 (1964).

(9) Attention has recently been drawn to the importance and possibly widespread occurrence of nonrigidity among inorganic molecules (although the cases under discussion here were not specifically mentioned) by E. L. Mutterties, *Inorg. Chem.*, **4**, 769 (1965). There are also examples of purely organic nonrigid molecules, the case of bullvalene being perhaps the most impressive; *cf.* W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 751 (1963).

(10) Many of the results described here in detail were first reported in a lecture by F. A. Cotton to the Ninth Robert A. Welch Foundation Conference on Organometallic Chemistry, Nov 17, 1965.

(10a) Note Added in Proof. In the hope of establishing some generally acceptable terminology concerning molecules which undergo relatively rapid *intramolecular* rearrangements, such as the one discussed in this paper, we offer the following comments and suggestions. E. L. Muetterties (*Inorg. Chem.*, **4**, 769 (1965)) has proposed the term "sterically nonrigid" for some such molecules. W. von E. Doering and W. R. Roth (*Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963)) have used the term "fluxional structures" to describe molecules which are distinguished by more than one geometrically identical potential well, *e.g.*, bullvalene. The older term "valence tautomerism" does not apply to such phenomena generally, nor does it apply to intramolecular rearrangements such as planar–tetrahedral equilibria or to the trigonal bipyramidal–square pyramidal–trigonal bipyramidal rearrangements (in PCl_2F_3, $Fe(CO)_5$, etc.) which permute axial and equatorial positions, nor does it apply to the inversion motions in cyclohexane, amines, sulfides, etc. These allogonic rearrangements (*allo* meaning different and *gon* meaning angle), unlike that in bullvalene, do not involve breaking and re-forming of bonds, but only changes of angles. We therefore propose "stereochemically nonrigid" as a general term which includes all of the intramolecular rearrangements mentioned above. Subdivisions of stereochemical nonrigidity can then be made on the basis of equivalence or nonequivalence of potential wells, the origin of the barriers, and the equivalence or nonequivalence of the barrier heights.

Table I. Observed and Calculated Structure Factors

H	K	FOBS	FCAL
****L =		0******	
3	0	2363	-2023
4	0	254	-279
5	0	2304	2529
6	0	2942	2681
7	0	342	-315
8	0	4140	-4264
9	0	395	-447
10	0	1838	1717
11	0	3014	2788
12	0	1099	1081
13	0	1357	-1616
1	1	1552	1356
2	1	1739	-1217
3	1	4728	4073
4	1	840	958
5	1	1139	1003
6	1	1388	-1481
7	1	1101	-799
8	1	710	-657
9	1	399	-124
0	1	425	833
9	2	1586	1463
1	2	3022	3224
2	2	1757	-1548
3	2	1776	-1961
4	2	293	314
5	2	3608	3491
6	2	3952	4001
7	2	1029	-960
8	2	2103	-2132
9	2	1009	-1183
10	2	1572	1659
11	2	1760	1673
1	3	292	-496
2	3	300	611
3	3	2166	-1929
4	3	1583	-1592
5	3	930	-911
6	3	366	346
7	3	386	622
8	3	408	514
9	3	430	-372
10	3	453	-443
11	3	476	395
0	4	4134	4262
1	4	2220	2117
2	4	2311	-2189
3	4	3215	-3465
4	4	366	325
5	4	2465	2237
6	4	1124	1132
7	4	415	-391
8	4	1943	-2129
9	4	1286	-1400
10	4	1042	1048
11	4	1540	1827
1	5	749	-539
2	5	549	540
3	5	396	-465
4	5	1258	-1512
5	5	418	-434
6	5	432	818
7	5	447	551
8	5	464	-116
0	6	2393	2441
1	6	812	1037
2	6	1159	-1312
3	6	2301	-2426
4	6	446	-491
5	6	1292	1378
6	6	864	728
7	6	482	-506
8	6	1279	-1391
1	7	1055	1070
2	7	474	419
3	7	480	-91
4	7	487	-751
5	7	496	-398
0	8	515	640
1	8	515	399
2	8	802	-935
3	8	1323	-1400

H	K	FOBS	FCAL
4	8	530	-80
5	8	1202	1211
****L =		1******	
1	2911	2998	
1	4825	4661	
1	2725	3128	
1	446	-458	
1	1222	1133	
1	3357	-3091	
1	2796	-2685	
1	1973	-1705	
1	3583	-3934	
1	2280	2024	
1	696	-628	
1	3204	2572	
1	2332	2462	
1	390	221	
1	2072	2193	
1	2105	-1965	
1	423	-594	
1	1972	-1914	
1	1703	-1802	
1	807	635	
1	947	-822	
1	1839	1912	
1	499	586	
1	953	693	
1	1049	877	
2	1529	1146	
2	3414	-3508	
2	869	569	
2	633	-612	
2	3186	-3458	
2	1484	-1091	
2	900	-594	
2	2171	-1922	
2	1494	1326	
2	315	-161	
2	617	-352	
2	678	-170	
2	813	747	
2	761	513	
2	795	-610	
2	1159	-1190	
2	860	-738	
3	4065	-4368	
3	2208	-2596	
3	530	-259	
3	666	-643	
3	3636	3802	
3	2025	1961	
3	2453	2414	
3	2179	2013	
3	1067	-993	
3	964	-744	
3	3085	-3127	
3	2877	-3138	
3	621	-494	
3	667	-435	
3	2800	2873	
3	2857	3284	
3	2580	2631	
3	2009	1947	
3	422	-51	
3	450	-370	
3	1741	-1676	
3	1641	-1707	
3	1384	-1305	
3	1217	-1194	
3	489	8	
3	1052	890	
4	699	-753	
4	1624	-1653	
4	946	-793	
4	1633	-1669	
4	712	-658	
4	609	-573	
4	348	18	
4	363	-82	
4	1138	-1116	
4	1111	-676	
4	374	-197	
4	395	-96	

H	K	FOBS	FCAL
-7	4	1459	1330
-8	4	866	-810
-8	4	998	648
-9	4	952	-894
-9	4	891	-923
0	5	1942	-1903
1	5	2367	-2423
-1	5	656	29
2	5	666	572
-2	5	3499	3592
3	5	2090	3125
-3	5	2185	2140
4	5	900	739
-4	5	1454	-1492
-5	5	1808	-1886
-5	5	1643	-1638
6	5	1716	-1743
-6	5	424	-587
7	5	444	-277
-7	5	429	-58
8	5	922	663
-8	5	1153	1152
9	5	1729	1469
-9	5	473	526
10	5	498	67
-10	5	1969	-1732
11	5	984	-1022
1	3	859	-983
-1	3	870	-648
2	3	2533	2355
-2	3	307	-133
3	3	328	-126
-3	3	1194	1139
4	3	2313	-2054
-4	3	1234	1146
5	3	364	481
-5	3	1093	-994
6	3	385	94
-6	3	372	-942
7	3	407	9
-7	3	393	-212
8	3	429	844
-8	3	415	-494
9	3	452	593
0	4	2495	2500
-1	4	2730	-2715
1	4	3555	3817
-2	4	3889	-3964
2	4	359	303
3	4	2496	-2665
-3	4	1091	-995
4	4	2459	-2463
-4	4	2748	2751
5	4	1025	793
-5	4	2305	2169
6	4	2166	2432
-6	4	405	11
7	4	1367	1626
-7	4	1789	-1897
8	4	955	-1379
-8	4	1762	-1809
9	4	1907	-2138
-9	4	464	702
-10	4	1916	1918
0	5	397	-63
-1	5	397	-30
1	5	397	210
-2	5	401	-82
2	5	404	373
-3	5	408	3
3	5	411	518
-4	5	418	383
4	5	425	-545
-5	5	429	-555
5	5	435	-91
-6	5	443	-847
6	5	453	168
-7	5	460	-604
7	5	467	59
-8	5	1025	1269
8	5	443	-494
-9	5	2298	2608
9	6	1608	-1610

H	K	FOBS	FCAL
1	1	1166	-1043
-1	1	351	503
2	1	305	-74
-2	1	1367	1051
3	1	769	-763
-3	2	242	-253
4	2	1625	-1309
-4	2	3132	-3650
5	2	1770	2014
-5	2	7909	-7999
6	2	1806	-1989
-6	2	3086	-2697
7	2	3111	-2855
-7	2	3566	3293
8	2	334	315
-8	2	4678	4331
9	2	3736	3879
-9	2	1554	-1504
10	2	1656	1724
-10	2	2523	-2215
11	2	1754	-1795
-11	2	1181	-1043
1	2	2423	-2551
-1	2	954	996
2	2	1314	-1310
-2	2	1933	1696
3	3	598	-397
-3	3	859	-983
4	3	870	-648
-4	3	2533	2355
5	3	307	-133
-5	3	328	-126
6	3	1194	1139
-6	3	2313	-2054
7	3	1234	1146
-7	3	364	481
8	3	1093	-994
-8	3	385	94
9	3	372	-942
-9	3	407	9
10	3	393	-212
-10	3	429	844
11	3	415	-494
-11	3	452	593
12	3	2495	2500
-12	3	2730	-2715
1	4	3555	3817
-1	4	3889	-3964
2	4	359	303
-2	4	2496	-2665
3	4	1091	-995
-3	4	2459	-2463
4	4	2748	2751
-4	4	1025	793
5	4	2305	2169
-5	4	2166	2432
6	4	405	11
-6	4	1367	1626
7	4	1789	-1897
-7	4	955	-1379
8	4	1762	-1809
-8	4	1907	-2138
9	4	464	702
-9	4	1916	1918
10	5	397	-63
-10	5	397	-30
11	5	397	210
-11	5	401	-82
1	5	404	373
-1	5	408	3
2	5	411	518
-2	5	418	383
3	5	425	-545
-3	5	429	-555
4	5	435	-91
-4	5	443	-847
5	5	453	168
-5	5	460	-604
6	5	467	59
-6	6	1025	1269
7	6	443	-494
-7	6	2298	2608
8	6	1608	-1610

H	K	FOBS	FCAL
2	6	446	398
-3	6	449	-701
3	6	1398	-1551
-4	6	941	1102
4	6	1472	-1255
-5	6	1293	1491
5	6	474	143
-6	6	481	247
6	6	1517	1575
-7	6	1172	-1258
7	7	997	-918
1	7	1116	929
2	7	1266	1433
****L =		3******	
2	1	2825	-2687
3	1	1160	1516
-4	1	5265	-4300
4	1	4281	4566
5	1	560	835
-5	1	362	395
6	1	3701	-2998
-7	1	2418	2100
7	1	2180	-2166
-8	1	433	445
8	1	428	329
-9	1	2069	-1859
9	1	1404	1335
-10	1	2502	-2033
10	1	1594	1671
-11	1	533	107
11	1	1877	1576
-12	1	1136	1235
12	2	303	422
1	2	3087	3248
-1	2	3233	2557
2	2	637	-251
-2	2	1184	956
3	2	1573	-1503
-3	2	1403	-886
4	2	1726	1248
-4	2	364	398
5	2	1521	1431
-5	2	557	645
6	2	452	814
-6	2	424	-223
7	2	483	-343
-7	2	455	-101
8	2	514	-100
-8	2	485	259
9	2	545	-306
-9	2	516	-621
10	2	1149	1036
-10	3	373	-513
0	3	4105	-4390
-1	3	3611	3708
1	3	768	-798
-2	3	2482	2490
2	3	1428	1590
-3	3	395	-624
3	3	3077	3498
-4	3	5523	-5609
4	3	458	960
-5	3	2957	-2847
5	3	2044	-1945
-6	3	2497	2187
6	3	2334	-2577
-7	3	3576	3502
7	3	539	375
-8	3	513	429
8	3	2127	2432
-9	3	1532	-1277
9	4	2025	2132
-10	4	440	-387
10	4	435	109
-11	4	1225	-979
11	4	441	573
-12	4	1078	655
12	4	451	443
1	4	1191	1258
-1	4	531	-391
2	4	1836	1635
-2	4	523	159

H	K	FOBS	FCAL
4	4	503	798
-1	4	547	1156
2	4	525	446
-2	4	572	-280
3	5	494	305
-3	5	2147	-2105
4	5	2511	2503
-4	5	2072	-2172
-6	5	2512	2360
-7	5	1932	1884
-8	5	506	-85
-9	5	1913	1960
0	5	1463	-1726
1	5	547	118
-1	5	1664	-1616
2	5	1476	-1752
-2	5	548	551
3	5	1761	-1939
-3	6	954	946
4	6	554	-25
-4	6	560	142
5	7	606	791
-5	7	1494	1334
6	7	615	17
-6	7	1764	-1502
7	****L =		4******
-7	0	3668	3727
8	0	458	-908
-8	0	4106	-4350
9	0	3217	2801
-9	0	3162	-3411
10	0	3274	3360
-10	0	2083	2072
11	0	1767	-1774
-11	0	3033	3111
12	0	3763	-3868
-12	0	1289	1159
1	0	335	330
-3	0	390	-431
0	0	2295	2182
1	0	871	-841
-1	0	1217	1223
2	0	439	134
-2	0	1214	-912
3	0	1606	1244
-3	0	2163	-1235
4	0	900	847
-4	0	1632	1423
5	1	965	1078
-5	1	1372	1597
6	1	295	-10
-6	1	925	-961
7	1	2061	-2010
-7	0	915	-777
0	1	1607	1537
2	2	775	-660
-1	2	1608	1664
-2	2	4579	-4470
-3	2	3242	3621
****L =		5******	
6	0	1873	-1858
1	1	1666	1548
-1	1	3601	3537
2	2	3185	-3029
-2	2	5524	5567
3	2	1175	-1266
-3	2	1073	1018
4	2	2114	2[illegible]
-4	2	2291	-2259
5	2	2728	2763
-5	2	1933	-1767
6	2	1081	896
-6	2	500	739
7	2	849	-687
-7	2	2365	2384
8	2	1602	-1627
-8	2	894	644
9	2	451	-283
-9	2	845	-494
10	2	1291	1286
-10	2	1092	-1217
0	3	2223	-2362
1	3	281	-253
-1	3	951	-926

H	K	FOBS	FCAL
2	3	805	652
-2	3	1780	1694
3	3	305	130
-3	3	1293	1093
4	3	1171	-1071
-4	3	302	290
5	3	1115	756
-5	3	354	-428
6	3	838	567
-6	3	1160	1004
7	3	1331	-1330
-7	3	423	-539
11	4	3153	3228
8	4	1955	-2292
0	4	2482	2639
1	4	1573	-1659
-1	4	1900	-1476
2	4	1442	1435
-2	4	2599	-2999
3	4	3574	3661
-3	4	909	-1157
4	4	1499	1205
-4	4	1365	1262
5	4	2034	-2023
-5	4	1621	1812
6	4	2403	-2465
-6	4	1038	843
7	4	401	-53
-7	4	930	-1318
8	4	1391	1379
0	4	926	-1059
10	4	1160	1290
0	4	484	269
1	4	458	-548
-1	4	1011	974
2	4	1322	-1393
-2	4	957	-718
3	4	742	731
-3	4	993	-700
4	4	1437	1049
-4	4	1441	-1371
5	4	1801	1719
0	5	1173	1007
4	6	814	-546
1	6	420	-581
2	6	759	519
-2	6	1717	-1644
3	6	1620	1521
4	6	1433	-1373
5	6	427	377
6	6	452	-61
7	6	1856	-1788
8	6	1682	1585
0	7	1025	-941
****L =		6******	
7	0	1130	-775
2	7	1110	674
3	7	1759	-1544
4	7	1295	-932
5	8	1102	759
-5	0	1952	-1924
6	0	4326	-4167
-7	0	411	277
8	0	898	-1114
-8	0	2038	2303
9	0	2635	2104
-9	0	1578	1439
10	0	2004	-1791
-10	0	820	-763
11	0	998	-835
-11	0	1273	-1562
1	1	419	157
2	1	1241	1194
-2	1	1031	-877
3	1	2059	-2111
-3	1	2132	-1842
4	1	1535	2475
-4	1	653	534
5	1	1781	-1699
-5	1	770	-1208
6	1	3030	-1552
-6	1	3339	-3808
0	1	513	92
1	1	464	-2529
-1	1	2009	1501
2	1	1389	379
-2	2	1452	1358
3	2	1124	-973
-3	2	1588	375

H	K	FOBS	FCAL
5	2	327	-238
-5	2	296	-548
6	2	353	-455
-6	2	1824	-1581
7	2	381	-233
-7	2	410	-366
-8	2	366	170
9	2	439	287
-9	2	1115	-934
10	2	468	11
-10	2	1062	-1335
-11	2	1955	-2292
1	3	2760	2519
1	3	2097	-1982
0	3	1841	1815
1	3	4205	-3652
-1	3	680	352
2	3	398	534
-2	3	4309	-3566
3	3	2920	2342
-3	3	3877	-3026
4	3	2873	2443
-4	3	407	150
5	3	468	-269
-5	3	4305	3466
-6	3	1352	-1308
-7	3	2961	2312
-8	3	988	-1061
-9	3	548	505
-10	3	1431	1114
-11	4	1518	1236
-2	4	1372	-1734
6	4	1842	-1431
0	4	417	-1422
1	4	446	-375
-1	4	1474	-335
2	4	462	-135
-2	4	1516	615
3	4	492	-695
-3	5	2851	-759
-4	5	1368	-2210
5	5	1675	503
-5	5	1849	-1184
6	5	1902	1749
-6	5	969	1449
7	5	1376	197
-7	5	1405	-1465
8	5	586	-1058
-8	5	1490	340
****L =		7******	
2	0	3360	3673
3	0	281	441
5	0	2745	-2701
-5	0	3308	-3359
6	0	2653	-2390
-6	0	1952	-1924
-7	0	4326	-4167
8	0	411	277
-8	0	2802	-2965
-9	0	853	-867
9	1	1487	-1536
-4	1	1042	1148
4	1	1230	1421
-5	1	1135	1416
6	1	2134	2298
-7	1	1389	1552
7	1	1291	852
-8	1	1579	-1739
8	1	1061	-2051
-9	1	2295	-1867
9	2	2174	-1889
-10	2	1123	1083
0	2	1511	1209
-1	2	1344	1618
1	2	2161	1891
-2	2	1461	-1166
2	2	1482	-1055
-4	2	1470	1219
-5	2	991	-1112
4	2	2066	1710
-7	2	1152	-1285

H	K	FOBS	FCAL
0	5	1892	2321
-1	5	947	895
2	5	1121	-1309
-2	5	1172	-1020
3	5	1625	-1458
-3	5	1097	-1203
5	5	1116	1039
-5	5	1684	1695
6	5	1266	1029
8	5	1245	-1123
-8	5	1853	-1883
****L =		8******	
3	0	1230	1482
0	0	1879	2146
-5	0	2237	-1635
7	0	1713	1573
8	0	1286	1256
-8	0	1525	1621
9	0	2163	1733
-10	0	1248	-1553
-11	0	1629	-1599
0	2	2236	-2575
1	2	1257	-1400
3	2	2819	2782
-3	2	1971	2041
4	2	2384	2506
-4	2	988	-1175
-5	2	2199	-1959
6	2	1528	-1566
-7	2	1107	1436
8	2	1543	1435
-8	2	2147	2324
5	4	1782	-1871
1	4	1506	-1526
-2	4	2078	1734
1	4	1676	1352
-3	4	1648	-1296
6	4	1343	-1153
-7	4	1380	1355
0	4	1120	-1380
1	6	1121	-1199
-2	6	1117	1093
****L =		9******	
0	1	1187	1641
1	1	1523	1857
2	1	740	476
-3	1	1786	-713
1	1	1096	-1388
-4	1	1421	2093
4	1	1665	-1549
-6	1	1271	-56
6	1	1818	3468
-7	1	1187	-1427
1	1	1440	534
3	1	1376	-1128
0	3	1166	1766
-1	3	1060	-911
1	3	2128	2132
2	3	1789	-1817
2	3	1118	1190
-3	3	1470	-1357
3	3	1177	-1117
-4	3	796	772
4	3	1350	-1383
-5	3	1867	1740
6	3	1505	1264
7	3	1313	-1272
7	3	762	870
-8	3	890	-377
8	3	801	-814
9	3	944	866
0	3	975	-1127
-10	3	1177	1292
0	5	1222	1348
-1	5	1145	-981
1	5	1601	1436
-2	5	1282	-1340
2	5	1113	-993
-4	5	1098	1229
-5	5	1039	977
4	6	1069	992
-7	6	1152	-1285

at −78° followed by a slow vacuum sublimation (10 hr at 25° and 10 μ) onto a water-cooled probe gave pure crystalline (π-C_5H_5)Fe-$(CO)_2$(σ-C_5H_5). It decomposed very slowly to ferrocene, and samples several weeks old were repurified using the above procedure just prior to use.

Nuclear Resonance Measurements. These were made on solutions in carbon disulfide and in dimethyl ether in the temperature range −100 to +30°, using a Varian Associates A-60 spectrometer equipped with a low-temperature probe which was modified to permit operation as low as −100°.

Crystallographic Investigation. The crystals were small red monoclinic prisms. Precession and Weissenberg photographs showed that the unit cell is monoclinic, with the dimensions a = 12.53 ± 0.03, b = 7.50 ± 0.02, c = 11.29 ± 0.02 A, β = 98.0 ± 0.5°, V = 1061 ± 6 A³. The observed systematic absences $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$, identify the space group as $P2_1/c$. The approximate density is 1.5 g cm⁻³ which indicates four molecules per unit cell (d calcd, for Z = 4, 1.54 g cm⁻³).

A small crystal, of dimensions 0.25 × 0.15 × 0.25 mm, was mounted on the c axis and equiinclination Weissenberg photographs of the levels $hk0$–$hk9$ were recorded by the multiple film technique using Mo Kα radiation filtered through Zr foil. These data were collected at *ca.* 20° using approximately 30-hr exposures. Intensities were estimated visually by comparison with a set of timed exposures. Approximately 870 reflections were measured.

The low-angle unobserved reflections were assigned one-half the minimum observed intensity and Lorentz polarization corrections were applied. No absorption corrections were applied since μ was only 15.1 cm⁻¹. The coordinates of the iron atom were estimated from a Patterson synthesis[11] and used to calculate the structure factors for a Fourier synthesis.[11] At this point it was clear that the iron atoms occupied the general, fourfold equipoint of the cell so that no crystallographic symmetry requirements are imposed on the molecule. The σ-C_5H_5 ring and the two CO groups were located on this Fourier map. A new set of signs was then calculated using these atoms as well as the iron atom from which a second Fourier synthesis was prepared. On this Fourier, the positions of the remaining five carbon atoms were evident. Three cycles of full-matrix least-squares refinement[12] of all positional parameters, isotropic thermal parameters, and scale factors gave a residual ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.141 using unit weights. The small changes in positional parameters in the last cycle and the reasonable temperature factors suggested that satisfactory convergence had been attained. The observed and calculated structure factors are recorded in Table I. The atom parameters obtained are listed in Table II.

Table II. Fractional Atomic Coordinates and Isotropic Temperature Parameters[a,b]

Atom	x/a	y/b	z/c	B
Fe	0.1849 (2)	0.9917 (4)	0.4282 (2)	2.29 (9)
C_1	0.744 (2)	0.304 (3)	0.176 (2)	3.1 (5)
C_2	0.668 (2)	0.188 (3)	0.101 (2)	3.4 (5)
C_3	0.565 (2)	0.213 (3)	0.137 (3)	3.9 (5)
C_4	0.574 (2)	0.331 (4)	0.230 (3)	5.3 (6)
C_5	0.679 (2)	0.392 (4)	0.267 (3)	5.3 (7)
C_6	0.877 (2)	0.320 (3)	0.007 (3)	3.7 (5)
C_7	0.916 (2)	0.529 (3)	0.184 (2)	3.2 (5)
C_8	0.343 (2)	0.092 (3)	0.485 (3)	3.9 (5)
C_9	0.289 (2)	0.454 (3)	0.083 (3)	4.3 (6)
C_{10}	0.194 (2)	0.352 (3)	0.072 (3)	4.0 (5)
C_{11}	0.186 (2)	0.239 (4)	0.983 (3)	4.3 (5)
C_{12}	0.275 (2)	0.224 (3)	0.417 (3)	4.4 (6)
O_1	0.920 (1)	0.198 (2)	0.972 (2)	4.2 (4)
O_2	0.990 (1)	0.559 (2)	0.254 (2)	5.4 (4)

[a] Atoms numbered as in Figure 1. [b] Figures in parentheses are the standard deviations occurring in the last recorded figure of each datum.

It should be noted that owing to the instability of the substance some decomposition unquestionably occurred as the photographs were taken. This could lead to systematic errrors such that the estimated standard deviations of atomic parameters underestimate the true uncertainties.

(11) Patterson and Fourier syntheses were computed using MIFR-2, our version of the Sly–Shoemaker–van den Hende Fourier program for the IBM 7094.

(12) Using SFLSQ-3, a full-matrix least-squares refinement program for the IBM 7094 by C. T. Prewitt, MIT, 1962.

Results

Crystal Structure. The molecular structure is shown in Figure 1, which also gives the atom numbering scheme followed in Tables II–V.

Table III. Intramolecular Distance[a,b]

Fe–C_1	2.11 (2)	C_1–C_2	1.46 (3)
Fe–C_6	1.72 (2)	C_2–C_3	1.42 (3)
Fe–C_7	1.68 (2)	C_3–C_4	1.37 (4)
Fe–C_8	2.13 (2)	C_4–C_5	1.40 (4)
Fe–C_9	2.07 (3)	C_5–C_1	1.54 (4)
Fe–C_{10}	1.98 (3)	C_8–C_9	1.41 (4)
Fe–C_{11}	2.12 (3)	C_9–C_{10}	1.40 (3)
Fe–C_{12}	2.09 (2)	C_{10}–C_{11}	1.30 (4)
C_6–O_1	1.16 (2)	C_{11}–C_{12}	1.45 (4)
C_7–O_2	1.15 (3)	C_{12}–C_8	1.45 (4)

[a] In angstrom units; atoms numbered as in Figure 1. [b] Numbers in parentheses are standard deviations in A × 10².

Table IV. Intramolecular Angles[a,b]

Fe–C_1–C_2	112 (1)	C_1–C_2–C_3	108 (2)
Fe–C_1–C_5	113 (2)	C_2–C_3–C_4	109 (2)
Fe–C_6–O_1	174 (2)	C_3–C_4–C_5	114 (3)
Fe–C_7–O_2	174 (2)	C_4–C_5–C_1	103 (2)
C_1–Fe–C_6	89 (1)	C_5–C_1–C_2	107 (2)
C_1–Fe–C_7	92 (1)	C_8–C_9–C_{10}	107 (2)
C_6–Fe–C_7	96 (1)	C_9–C_{10}–C_{11}	113 (2)
		C_{10}–C_{11}–C_{12}	106 (3)
		C_{11}–C_{12}–C_8	107 (2)
		C_{12}–C_8–C_9	105 (2)

[a] In degrees; atoms numbered as in Figure 1. [b] Numbers in parentheses are standard deviations in degrees.

Table V. Mean Planes and Distances

1. Mean plane of π-C_5H_5 ring			
(a) Equation			
$0.511X - 0.708Y + 0.488Z - 0.546 = 0$			
(b) Distances of atoms from plane, A			
C_8	−0.01	C_{11}	−0.04
C_9	−0.01	C_{12}	+0.03
C_{10}	+0.03	Fe	1.70
2. Mean plane of σ-C_5H_5 ring			
(a) Equation:			
$0.621X - 0.760Y + 0.192Z - 0.482 = 0$			
(b) Distances of atoms from plane, A			
C_1	−0.02	C_4	−0.02
C_2	+0.02	C_5	+0.03
C_3	−0.01	Fe	−1.73

In the present context, it is the nature of the structure rather than its precise dimensional details which is of principal importance, and, most particularly, the structural relationship of the non-π-bonded C_5H_5 ring to the iron atom.

Clearly, this ring is present as a σ-C_5H_5 ring. It is the first such (σ-C_5H_5)-to-metal moiety to be structurally characterized in an X-ray study. The ring itself is planar to well within the experimental uncertainties (see Table V) and the three measurable bond angles about C_1 are 107, 112, and 113°. The C_1–Fe bond length, 2.11 ± 0.02 A, may be compared with the other reported Fe–C σ-bond lengths, namely that in $(OC)_2$-

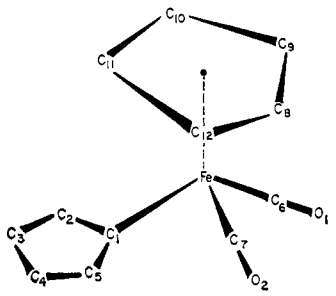

Figure 1. The molecular configuration in crystalline (π-C_5H_5)Fe-(CO)$_2C_5H_5$. Atoms are numbered as in Tables II–V.

Fe(π-$C_5H_4CH_2$)–Fe(CO)$_4$,[13] 2.12 A, those in (OC)$_3$-Fe[C(OH)=C(CH_3)(CH_3)C=COH]Fe(CO)$_3$,[14] and those in Fe$_2$(CO)$_6$($C_6H_5C_2H$)$_3$,[15] 2.01, 2.09, 2.10 A. Although the aptness of all of these comparisons is questionable since there are differences in formal oxidation states of the iron, differences in hybridization of the carbon atoms, and evidences of varying degrees of steric strain in the different molecules, the values are reasonably concordant. The carbon–carbon distances within this ring show some differences from the pattern expected for a cyclopenta-2,4-diene ring but the standard deviations are such that no significance can be attached to this, and the differences cannot be said to be certain.

The (π-C_5H_5)Fe part of the molecule has dimensions in good accord with those found for this grouping in numerous other cases.

The dimensions of the iron carbonyl groups are of interest in connection with questions of the metal radius and the Fe–CO bonding. The mean C–O distance, 1.16 ± 0.02 A, is entirely typical for metal carbonyls in general, and the deviations of the Fe–C–O angles from 180° are also not uncommon nor unexpected when linearity is not demanded by molecular symmetry.[16] The mean Fe–C distance, 1.70 ± 0.02 A, is shorter than those (~1.75 A) found in derivatives of what is formally Fe(I) and considerably shorter than those found in compounds of formally zero-valent iron, such as Fe(CO)$_5$[17] (1.80 A) and (C_5H_5)Fe(CO)$_3$[18] (1.80 A). This trend may be partly influenced by the differing numbers of CO groups competing for available iron dπ electrons, but probably reflects at least in part a tendency for the metal radius to decrease as the formal oxidation state increases.

From the Fe–C_1 distance (2.12 A), we estimate an Fe single bond radius of 1.35 A. Thus a single bond from iron to sp-hybridized C should have a length of *ca.* 2.05 A. The actual Fe–CO distances, averaging 1.70 A, therefore indicate considerable π character in the Fe–C bonds.[19]

(13) J. Meunier-Piret, P. Piret, and M. van Meerssche, *Acta Cryst.*, **19**, 85 (1965).
(14) A. A. Hock and O. S. Mills, *ibid.*, **14**, 139 (1961).
(15) G. S. D. King, *ibid.*, **15**, 243 (1962).
(16) S. F. A. Kettle, *J. Chem. Soc.*, 1661 (1965).
(17) J. Donohue and A. Caron, *Acta Cryst.*, **17**, 663 (1964).
(18) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).
(19) It is interesting to note that on comparing these results with those for the [Fe(CN)$_5$NO]$^{2+}$ ion[20] in which Fe–N = 1.63 A and the mean Fe–C distance is 1.91 A, it seems evident that while the Fe–N bond has a great deal of multiple bond character, the Fe–CN bonds have much less π character than do the Fe–CO bonds in this and other iron carbonyl compounds.
(20) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

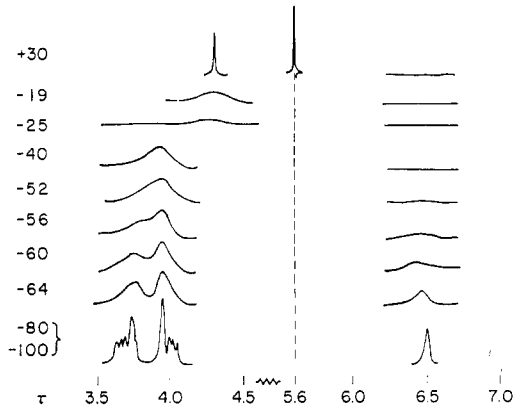

Figure 2. The proton magnetic resonance spectra of (π-C_5H_5)Fe-(CO)$_2C_5H_5$ in CS_2 at various temperatures. The dotted line represents the resonance position of the π-C_5H_5 protons at each temperature. The amplitude of the +30° spectrum is shown ×0.1 relative to the others.

Proton Magnetic Resonance Spectra. The proton nmr spectra of (π-C_5H_5)Fe(CO)$_2$(C_5H_5) in CS_2 solution at various temperatures from +30 to −100° are displayed in Figure 2. The spectrum at +30° shows two resonances, one at τ 5.60 and another of essentially the same integrated intensity, though noticeably broader, at τ 4.30. These results are the same as those previously reported by Piper and Wilkinson[4] at ~25°. The line at τ 5.60 can be assigned[21] to the π-C_5H_5 protons on the basis of its chemical shift alone, but the low-temperature spectra provide conclusive evidence for this.

As the temperature is lowered, the low-field signal broadens and eventually collapses completely at about −25°. As the temperature drops further two new bands appear. One due to the protons on the four carbon atoms not bonded to the iron atom begins as a single broad, asymmetric band at τ ~4 but separates into two bands, each of relative intensity two, this separation becoming clearly evident at ~60°. The other peak of relative intensity 1 is fairly broad (width at half-height, ~5 cps) even at ~100° and centered at τ 6.5. During the course of these changes, the peak at τ 5.60 retains its position, shape, and relative intensity of 5, thus confirming its assignment to the π-C_5H_5 group.

In addition, and of great significance (see Discussion), is the fact that the two halves of the absorption at τ ~4 vary differently with temperature. The portion at higher τ is higher and narrower at intermediate temperatures, and in the limiting spectrum (that which is reached at −70° and remains essentially unaltered down to −100°) this half shows somewhat better resolved fine structure.

The behavior of the spectrum in dimethyl ether as a function of temperature was essentially identical with that in carbon disulfide except for slight differences in τ values. In particular, the absorption envelopes in the two solvents at each temperature were essentially identical, indicating that there is no specific solvent dependence of the rearrangement process.

Discussion

We believe that the X-ray and nmr results described above clearly show that the molecular configuration of

(21) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

lowest potential energy for this molecule is essentially the one found in the crystal, that is, one in which the non-π-bonded cyclopentadienyl ring is bound through a normal iron-to-carbon σ bond. The stereochemical nonrigidity of the molecule as manifested in the proton nmr spectrum observed at room temperature and above is then a consequence of a relatively rapid shifting of the iron-to-carbon σ bond from one carbon atom of the ring to another, in complete accord with the original suggestion of Piper and Wilkinson. However, the manner in which the shift takes place remains to be specified. While this is not an easy task, we believe the data permit us to draw some definite conclusions. The question we wish to ask is the following: what is the metal-to-ring configuration in the transition state for the predominant shift mechanism? It is not, *a priori*, impossible that there might be two or more mechanisms which contribute significantly to the net result, but, as will be seen, a single process seems to be predominant.

In considering this problem, the detailed behavior of the absorption at $\tau \sim 4$ between ~ -40 and $\sim -70°$ as well as its final, constant character between $\sim -70°$ and $\sim -100°$ will be of critical importance. This absorption is due to the two pairs of protons on the carbon atoms other than that bound to the metal atom. Those in each pair should be instantaneously equivalent and should constitute the A_2 and B_2 members of an HA_2B_2 system. We shall specify the A_2 nuclei as those on the carbon atoms α to the unique carbon atom of the σ-C_5H_5 ring.

In the limit of $J_{HA} = J_{HB} = 0$ the A_2B_2 resonance should be symmetrical, the two halves being mirror images,[22] as in thiophene.[23] However, when $J_{HA} \gg J_{HB} \approx 0$, the A_2 portion of the A_2B_2 absorption would be expected to exhibit additional fine structure or, depending on the exact value of J_{HA} relative to J_{AB}, perhaps only a broadening of its structure. In the present case we may infer from the width ($\sim$5 cycles) of the H resonance at -70 to $-100°$ that J_{HA} is about 2 cycles. We would thus expect this to introduce only broadening rather than additional resolved fine structure in the A portion of the A_2B_2 mulitplet. Assuming that proton–proton coupling will attenuate with increasing distance,[24] we therefore conclude that the less well-resolved half of the observed A_2B_2 resonance corresponds to the A protons. In the present case, this is the half at lower τ.

We believe there are five mechanisms which might reasonably be considered for the rearrangement process. The first is an intermolecular one, proceeding either by dissociation or by a bimolecular exchange. However, the unsymmetrical manner in which the resonances collapse rules this out conclusively.

There are then four different intramolecular processes, which are indicated diagramatically in Figure 3. The path indicated in Figure 3a, which borders on being a dissociative process, would presumably have a very high activation energy and is rejected for this reason. The remaining three paths might all preserve substantial

(22) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(23) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, 1962, Spectrum No. 52.

(24) While this assumption cannot perhaps be defended as a universal rule, it seems reasonable and has empirical justification. For example,[21] in (π-C_5H_5)$Fe(CO)_2$(σ-allyl) this is the case.

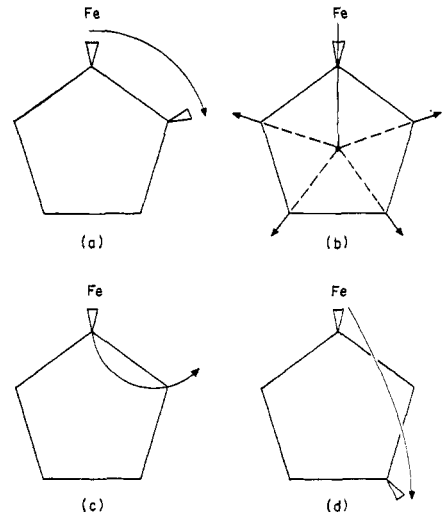

Figure 3. Diagrams showing four possible intramolecular paths leading to the nmr equivalence of the σ-C_5H_5 protons at room temperature.

bonding of the ring to the metal atom and are thus likely to have plausible activation energies. Mechanism b, however, can also be ruled out because it involves a stage in which all protons become equivalent. This in turn would necessitate symmetrical collapse of the spectrum in contradication to what is observed. This path might, however, be one leading to the irreversible decomposition of the compound to ferrocene, a process which occurs slowly even at low temperatures and more rapidly at high temperatures.

Thus, we have reduced the problem to distinguishing between paths c and d. In order to do so, we must observe in detail how the protons are permuted among the three environments, H, A, B, by the two paths. This is illustrated symbolically as follows.

$$\begin{bmatrix} A \\ H \\ A \\ B \\ B \end{bmatrix} \xleftarrow{\text{path c}} \begin{bmatrix} H \\ A \\ B \\ B \\ A \end{bmatrix} \xrightarrow{\text{path d}} \begin{bmatrix} B \\ A \\ H \\ A \\ B \end{bmatrix}$$

It will be noted that in each case all protons but one change environment. The difference lies in the fact that for path c the unchanged environment is of type B, while for path d it is of type A. The consequences of these observations are that for path c the A resonance should collapse most rapidly with increasing temperature, whereas for process d the B resonance should collapse soonest, since the averaging depends inversely on the lifetime of a nucleus in a given environment. The observed unsymmetrical collapse of the low-field resonance is clearly compatible with paths c and d. However, since the resonance which collapses most rapidly has been shown on the basis of the limiting low-temperature spectrum to be most likely due to the A protons, we conclude that path c, in which there is a 1,2 shift, is the major path for rearrangement.

The intermediate point in this path could be thought of as one in which the π-electron density of the ring is arranged in a two-center π bond through which the ring is bound to the iron and an allyl anion distribution over the other three carbon atoms. This point in the path may actually constitute a saddle point on the

potential energy *vs.* reaction coordinate graph, with the barrier to rearrangement being slightly higher than the energy difference between this structure and the ground structure.

Since the iron atom in $(\pi\text{-}C_5H_5)Fe(CO)_2$ has only one vacant σ orbital in its valence shell, the intermediate state in this process is consistent with the semiempirical rule which accords maximum stability to a 36-electron configuration for the metal atom in such compounds. In the 1,3 shift, on the other hand, the intermediate stage would involve a free C–C double bond and a bound π-allyl group, the latter having two more than the required number of electrons, with the least stable pair occupying a π-MO not symmetrically suited to overlap with the metal σ orbital.

It is interesting to compare the system studied here with the results recently reported by Fritz and Kreiter[25] for some cyclopentadienyl derivatives of the group four metals. In these cases the rate of the rearrangement process is so slow that it can only be observed in the form of a collapse of the σ-cyclopentadienyl spectrum to a single line at temperatures above room temperature for the silicon and germanium compounds, although for tetracyclopentadienyltin the process is rapid and only a single proton resonance line is observed even at $-60°$. These authors suggested a 1,2-shift mechanism, but no positive experimental evidence was offered to support this as against other possibilities such as those we have considered. The arguments presented here concerning $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$ can in principle be applied to these cases, but the data reported are insufficient actually to do so.

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Hydrogen Bridge Bonding in the $[M_2H(CO)_{10}]^-$ Anions (M = Cr, Mo, W)[1,2]

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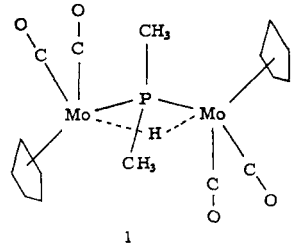
Received June 6, 1966

Abstract: Convenient syntheses have been developed for the $[M_2H(CO)_{10}]^-$ and $[M_2(CO)_{10}]^{2-}$ series of anions and the two series connected by an acid–base relationship. The formation of the mixed complexes $[MM'H(CO)_{10}]^-$ has been detected by proton nmr in statistically determined scrambling reactions involving pairs of the $[M_2H(CO)_{10}]^-$ anions, or pairs of the group VI metal hexacarbonyls. Infrared and proton nmr studies favor a symmetrical hydrogen-bridged structure for $[M_2H(CO)_{10}]^-$ in agreement with a recent X-ray structural investigation of $[(C_2H_5)_4N][Cr_2H(CO)_{10}]$.[17] The $[M_2(CO)_{10}]^{2-}$ series of complexes has been found to contain bridging carbonyl groups and is thus presumably isomeric with the complexes previously reported in the literature.[4,5]

Previous investigations of the anionic carbonyl complexes of the group VI metals have been carried out almost entirely by Behrens and his co-workers and, in a series of papers, they have reported the species $[M(CO)_5]^{2-}$,[3–5] $[MH(CO)_5]$,[3,4] $[M_2(CO)_{10}]^{2-}$,[4,5] $[M_2H(CO)_{10}]^-$,[4–6] and $[M_3(CO)_{14}]^{2-}$.[4,7] The structure of most of these anions, however, remains in doubt owing to the lack of spectroscopic and other physical data. In addition, many of the compounds were synthesized under unusual conditions (for example, in liquid ammonia at elevated temperatures) so that the complexes are not readily accessible for further study.

Our interest in the group VI carbonyl anions arose from a study of the complex $[(C_5H_5)_2Mo_2H(P(CH_3)_2)(CO)_4]$[8] which has recently been shown by Doedens and Dahl[9] to have structure **1**, although the position



1

of the unique hydrogen was not detected by X-rays. The two molybdenum atoms have identical stereochemical environments, each possessing the "3–4" type of coordination previously found in $[C_5H_5Nb(CO)_4]$[10] and $[C_5H_5Mo(CO)_3]_2$.[11] In $[(C_5H_5)_2Mo_2H(P(CH_3)_2)(CO)_4]$, however, only three of the four basal coordination positions are occupied by ligands which are visible to X-rays, and it is presumed that a bridging hydride ligand occupies the fourth position, thus filling the vacant coordination site of both metal atoms. In such a complex, it is not clear whether or not the hydride ligand plays an important role in binding the two metal atoms together, owing to the simul-

(1) Presented in part at the Second International Organometallic Symposium at Madison, Wis., Aug 29–Sept 3, 1965.
(2) Throughout this paper, M (or M′) = Cr, Mo, and W.
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