

When the reaction product was prepared as a solid and then dissolved in acetonitrile, the major absorption was found at  $-54$  ppm. These results indicate that

**2** and **3** are in equilibrium in acetonitrile, but the equilibrium lies far toward **3** which is of course in agreement with the conductivity data.<sup>12</sup>

## Stereochemically Nonrigid Organometallic Molecules. XVII.<sup>1</sup> The Crystal and Molecular Structure of Bis(cyclooctatetraene)triruthenium Tetracarbonyl<sup>2</sup>

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*Received June 27, 1968*

**Abstract:** The crystal and molecular structures of the fluxional molecule bis(cyclooctatetraene)triruthenium tetracarbonyl,  $(C_8H_8)_2Ru_3(CO)_4$ , have been determined from 1056 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the orthorhombic space group  $P2_12_12_1$  with four molecules in a unit cell of dimensions  $a = 9.737$  Å,  $b = 12.591$  Å, and  $c = 15.268$  Å ( $\rho_{obsd} = 2.18$  g cm<sup>-3</sup>;  $\rho_{calcd} = 2.21$  g cm<sup>-3</sup>). The structure, excluding hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional unweighted  $R$  factor of 4.07%. The molecules are dissymmetric; by taking into account anomalous dispersion by the ruthenium atoms, the correct enantiomorph has been selected for the crystal studied. Each molecule contains a triangle of Ru atoms (metal-metal distances of 2.782 (2), 2.928 (2), and 2.947 (2) Å), similar to that in  $Ru_3(CO)_{12}$ , and two cyclooctatetraene rings, each bound to a pair of ruthenium atoms. The structure is in accord with the mass spectral evidence for the existence of a metal atom cluster and accounts for the observed characteristic infrared spectrum in the CO stretching region. The bonding of the rings to pairs of metal atoms is extraordinary and cannot be related to any single type of olefin-metal interaction known. Instead it may be described as about halfway between two known and more-or-less symmetrical orientations for a  $(C_8H_8)_2M_2$  system. Thus the exceptional deformability which might be expected for a fluxional molecule along the reaction coordinate of its rearrangement pathway is strikingly illustrated.

Among the various products that have been isolated and characterized from the reaction of  $Ru_3(CO)_{12}$  with cyclooctatetraene (COT),<sup>4-7</sup> there is one which is produced exclusively when the process is carried out in refluxing octane. The crystalline substance so obtained is shown by elemental analysis and mass spectrum to be  $C_{16}H_{16}Ru_3(CO)_4$ , and its proton nmr spectrum at room temperature consists of one sharp peak. Consequently, the compound was expected to contain a metal atom cluster and is also a fluxional organometallic molecule, with the fluxional behavior implying retention of  $C_8H_8$  monocycles. It was obviously of interest to elucidate the structure of  $(COT)_2Ru_3(CO)_4$  in the solid state, and a single-crystal X-ray study was undertaken. The results of this study, which have previously been briefly communicated,<sup>8</sup> are reported here in full.

### Experimental Procedure

Crystalline  $C_{16}H_{16}Ru_3(CO)_4$  was prepared by the reaction of  $Ru_3(CO)_{12}$  with cyclooctatetraene in refluxing octane as described previously.<sup>6</sup> Optical examination showed the lustrous, red, air-stable crystals to be orthorhombic prisms, and preliminary Weissenberg ( $0kl$  and  $1kl$  levels) and precession ( $h0l$ ,  $h1l$ ,  $hk0$ , and  $hk1$  levels) photographs indicated Laue symmetry  $mmm$ , with slight deviations from this symmetry attributable to anomalous dispersion effects and suggesting crystal point group 222. The observed systematic absences ( $h00$  for  $h \neq 2n$ ,  $0k0$  for  $k \neq 2n$ , and  $00l$  for  $l \neq 2n$ ) indicated the unique choice of the orthorhombic space group  $P2_12_12_1$ . The unit cell dimensions, determined with copper radiation ( $\lambda K\alpha_1$  1.5405 Å,  $\lambda K\alpha_2$  1.5443 Å) by a method described elsewhere,<sup>9</sup> are  $a = 9.737 \pm 0.005$  Å,  $b = 12.591 \pm 0.007$  Å, and  $c = 15.268 \pm 0.008$  Å. The observed density of 2.18 g cm<sup>-3</sup>, determined by flotation, agrees with the calculated density of 2.21 g cm<sup>-3</sup> for a formula weight of 623.6,  $Z = 4$ , and a unit cell volume of 1871.8 Å<sup>3</sup>.

Intensity data were collected on a General Electric quarter-circle automated XRD-6 diffractometer equipped with a Datex control unit. A crystal of approximate dimensions  $0.2 \times 0.2 \times 0.3$  mm was so aligned that its  $a$  axis coincided with the  $\varphi$  axis of the instrument. The distances from the crystal to the source and from the crystal to the circular screening aperture ( $2^\circ$ ) were 5.73 and 7.05 in., respectively. Mo  $K\alpha$  radiation, filtered by zirconium foil, was used to measure 1165 independent reflections lying within one octant of a sphere in reciprocal space corresponding to  $d$  spacings  $\geq 1$  Å. The intensities were measured with a scintillation counter with the pulse height discriminator set to receive 95% of the Mo  $K\alpha$  radiation with the window centered on the Mo  $K\alpha$  peak. The data were collected using a coupled  $\omega/2\theta$  scan technique at a  $2\theta$  scan rate of  $2^\circ/\text{min}$ . The peak counts,  $P$ , were obtained from a  $2\theta$  scan of  $1.33^\circ$

(1) Part XVI: F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 5418 (1968).

(2) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society and by the National Science Foundation under Grant No. GP-7034X.

(3) J. F. Norris Predoctoral Fellow, 1967-1968.

(4) M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967).

(5) W. K. Bratton, F. A. Cotton, A. Davison, J. W. Faller, and A. Musco, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

(6) F. A. Cotton, A. Davison, and A. Musco, *J. Am. Chem. Soc.*, **89**, 6796 (1967).

(7) F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968).

(8) M. J. Bennett, F. A. Cotton, and P. Legzdins, *ibid.*, **89**, 6797 (1967).

(9) M. J. Bennett, F. A. Cotton, and J. Takats, *ibid.*, **90**, 903 (1968).

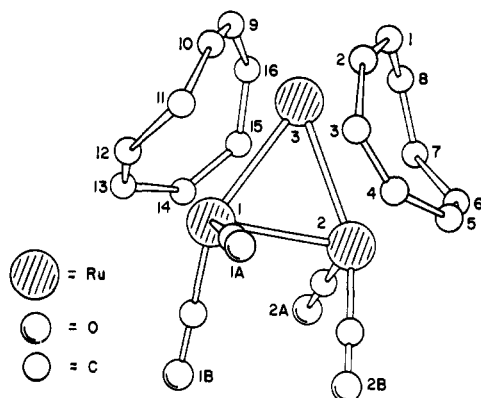


Figure 1. The molecular structure projected on the  $ab$  plane.

from  $2\theta_{\text{calcd}} - 0.67^\circ$  to  $2\theta_{\text{calcd}} + 0.66^\circ$ . Stationary background counts,  $B_1$ ,  $B_2$ , of 10 sec were taken at each of the limits of the scan. From these readings the intensity,  $I$ , assuming a linear change in background (or its equivalent) between the two limits of the scan, is given by  $I = P - 2(B_1 + B_2)$ . Periodic checks of three standard reflections, having no  $2\theta$  dependence, showed variations in intensities ( $\pm 2\%$ ) which were random with time and could be attributed to fluctuations in electronic circuits rather than to crystal decomposition. No appreciable variations in the intensities of the  $h00$  reflections were observed as a function of crystal orientation. Moreover, an absorption calculation involving a representative portion of the data showed the transmission factors to range from 0.865 to 0.900, and absorption corrections ( $\mu = 17.3 \text{ cm}^{-1}$ ) were therefore not applied.

Four strong reflections which exceeded the linear response range of the counter were discarded, and statistically insignificant reflections (105) were rejected using the criteria (1)  $I \leq 0$  and (2)  $I < 3(P + [T_P/T_B]^2[B_1 + B_2])^{1/2}$ , where  $T_P$  is the peak counting time and  $T_B$  is the background counting time. The remaining 1056 reflections were corrected for Lorentz and polarization effects and a set of  $|F_o|^2$  and  $|F_c|^2$  values (on a relative scale) was thus obtained.

### Solution and Refinement of the Structure

A three-dimensional Patterson map revealed the expected triangle of ruthenium atoms, and the rest of the structure was solved by conventional least-squares and Fourier calculations. The atomic scattering factors used during this analysis were those of Cromer and Waber,<sup>10</sup> and the anomalous dispersion corrections, both real ( $\Delta f' = -1.37 e$ ) and imaginary ( $\Delta f'' = 1.09 e$ ) parts, which were applied to ruthenium scattering factors, were those given by Cromer.<sup>11</sup> The function minimized during the least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $|F_o|$  is the observed structure amplitude,  $|F_c|$  is the calculated structure amplitude, and  $w$  is the weighting factor.

Four cycles of full matrix least-squares refinement of scale factor, atomic coordinates, and isotropic thermal parameters for all atoms led to a discrepancy index of  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.053$ . The weighted residual,  $R_2 = \{\sum w[|F_o| - |F_c|]^2 / \sum w|F_o|^2\}^{1/2}$ , using unit weights was 0.073. At this point an experimental weighting scheme similar to that of Doedens and Ibers<sup>12</sup> ( $w = [\sigma(F)]^{-2}$ ) was introduced, and the ruthenium atoms were assigned anisotropic temperature factors of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Two final cycles of refinement of positional and thermal parameters for all atoms resulted in convergence with  $R_1 = 0.041$  and  $R_2 = 0.058$ .

(10) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(11) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(12) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). Our weighting scheme differs only in that  $p = 0.045$ .

For an acentric space group  $|F(hkl)| \neq |F(\bar{h}\bar{k}\bar{l})|$  when the effects of anomalous dispersion are important (*i.e.*, when  $\Delta f''$  is appreciable). In particular, for  $P2_12_12_1$ ,  $\{|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})| = |F(h\bar{k}l)| = |F(hk\bar{l})|\} \neq \{|F(\bar{h}\bar{k}\bar{l})| = |F(\bar{h}k\bar{l})| = |F(h\bar{k}l)| = |F(hkl)|\}$  under such conditions, and it was thus necessary to test both enantiomeric structural solutions. In the absence of a complete data set the Hamilton  $R$ -factor test<sup>13a</sup> may be employed for the determination of absolute configuration on the basis of refinement of both structural models. Therefore, the structural solution A (the one just discussed, having atom positional coordinates  $x, y, z$ ) and one of the alternative solutions, B (with positional coordinates  $-x, y, z$ , resulting from reflection of the original structure in the (100) plane), were each refined in the same manner. The latter structure was accepted as the correct configuration because it converged to discrepancy indices  $R_1 = 0.0407$  and  $R_2 = 0.057$ . If these discrepancy indices for the two structures are used to evaluate the structures as hypotheses of one degree of freedom using the  $R$ -factor test, then structure B is validated at the 99.5% confidence level. In the nonpolar space group  $P2_12_12_1$ , no first-order errors should occur in the coordinates of the incorrect structural solution,<sup>13b</sup> and in this case none were found; no criterion of correctness is provided by molecular dimensions. Thus, by taking into account anomalous dispersion by the ruthenium atoms, the absolute configuration of the  $(\text{COT})_2\text{Ru}_3(\text{CO})_4$  molecule has been determined for the crystal studied. All subsequent discussion pertains to structure B.

During the final cycle of refinement, no parameter shifted more than one-eighth of its estimated standard deviation. The principal features of a final difference Fourier map computed at this point were (1) peaks of 0.88 and 0.86  $e/\text{\AA}^3$  in the vicinity of oxygen atoms  $\text{O}_{1B}$  and  $\text{O}_{2B}$  (Figure 1), (2) peaks of 0.72–0.55  $e/\text{\AA}^3$  which could be attributed to anisotropic motion of other atoms in the carbonyl moieties, and (3) peaks less than 0.50  $e/\text{\AA}^3$  which seemed indicative of unassigned electron density in the regions of the COT rings. Although some definite indications of the H atoms were present, these positions did not seem reliable enough to form a basis for refinement. The error introduced into the model by our neglect of the light atom anisotropic vibration was also reflected by the final standard deviation for an observation of unit weight being 1.591, instead of the expected value of unity. The experimental weighting scheme satisfied, within acceptable limits, Cruickshank's criterion,<sup>14</sup> and a comparison of the observed and final calculated structure amplitudes did not suggest that a correction for extinction was necessary.

The following programs for the IBM 7094 and 360 computers were used in the structure analysis and interpretation: (1) a modified version of "M.I.T. X-Ray Goniometer Package-MIXG-2," 1962, by D. P. Shoemaker; (2) general data reduction program, PMMO, by M. J. Bennett; (3) a modified version of Fourier analysis program, FORDAP, by A. Zalkin; (4) "Full-Matrix Crystallographic Least-Squares," SFLS5, 1966, by C. T. Prewitt; (5) "Molecular Geometry with Esti-

(13) (a) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965); (b) D. W. J. Cruickshank and W. S. McDonald, *ibid.*, **23**, 9 (1967).

(14) W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, p 113.

Table I. Observed and Calculated Structure Amplitudes ( $\times 10$ ) (in Electrons) for  $(C_8H_8)_2Ru_3(CO)_4$ 

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL																				
0	0	186C	1807	1	11	472	476	0	7	1067	1078	12	2	398	415	6	13	971	928	1	9	978	701	2	6	1360	1436	6	4	342	352	6	3	780	793	3	5	467	463				
2	0	186C	1807	2	11	704	674	1	7	905	884	5	0	3	616	505	0	14	395	377	3	9	720	753	6	6	216	207	7	4	539	554	7	3	319	315	6	5	251	249			
4	0	752	674	3	11	473	484	2	7	379	275	11	3	606	623	1	14	519	497	9	9	447	458	8	4	668	683	8	4	245	252	8	4	899	898	6	5	187	184				
6	0	702	774	4	11	312	287	3	7	954	959	2	3	606	605	2	14	164	142	5	9	402	438	6	6	560	564	9	4	275	277	9	3	350	280	7	5	187	194				
8	0	615	574	5	11	362	381	4	7	681	704	3	3	1104	1186	3	14	531	523	6	9	443	435	6	6	275	298	10	4	281	245	0	4	142	83	0	4	1005	1001				
10	0	671	699	6	11	454	581	5	7	1189	1235	4	7	1189	1235	5	3	316	368	9	9	837	856	8	6	422	425	0	5	232	250	1	4	462	407	1	1	1005	1011				
12	1	745	112	7	11	180	179	7	7	604	888	6	3	645	721	*****	3	*****	8	9	339	320	9	6	180	164	1	5	179	202	2	4	1167	1167	2	4	819	412					
2	2	259	233	8	11	250	190	7	7	864	888	6	3	1518	1561	1	0	2347	2416	9	9	520	526	10	6	431	430	2	5	593	584	3	4	810	813	3	4	508	495				
4	1	1078	1051	9	12	595	597	8	7	481	484	8	3	1097	1133	2	0	819	828	4	10	1049	1049	11	7	492	492	3	4	1032	1031	4	4	1049	1049	4	6	541	541				
6	1	1230	1376	10	12	745	737	7	7	867	861	9	3	776	873	0	0	1569	1546	10	10	1238	1237	1	7	248	277	4	5	903	914	5	4	473	641	5	4	456	491				
8	1	1837	1749	11	12	273	242	10	7	527	536	10	3	941	992	4	0	1223	1140	2	10	967	925	2	7	331	334	5	5	525	553	6	4	304	363	6	6	241	237				
10	1	1066	795	12	13	1221	1287	11	7	435	405	11	3	585	594	5	0	1232	1206	0	9	717	787	5	10	235	255	6	7	436	420	7	5	334	334	8	4	230	232	0	7	314	392
12	1	238	238	13	13	238	216	12	8	274	429	12	3	276	326	6	0	971	987	5	10	456	464	6	10	456	464	5	7	516	536	8	5	1196	1202	0	4	280	288	1	7	601	591
14	1	982	983	14	13	307	300	13	8	1094	1089	14	4	413	398	9	0	306	307	7	10	235	255	8	7	335	327	0	5	508	287	0	5	311	492	0	7	412	412				
16	1	951	600	15	13	439	465	14	8	597	576	15	4	436	495	10	0	400	422	8	12	316	316	7	7	269	237	0	6	1269	1242	1	5	704	701	3	7	392	357				
18	1	434	447	16	13	435	477	15	8	1083	1143	16	4	603	574	11	0	493	476	0	11	876	830	8	7	631	620	1	6	406	423	2	5	654	650	4	7	453	463				
20	1	485	442	17	13	224	173	16	8	379	404	17	4	503	609	0	1	1235	1064	1	11	172	186	9	7	750	758	2	6	149	159	3	5	520	548	4	6	233	194				
22	2	525	535	18	13	427	461	17	8	384	369	18	4	314	353	2	1	174	168	4	11	644	655	1	11	644	655	5	6	249	260	7	5	745	729	6	8	747	746				
24	2	577	547	19	14	522	511	18	8	269	230	19	4	274	297	3	1	1533	1475	5	11	398	349	2	8	524	534	6	6	444	423	9	5	659	652	3	8	406	415				
26	2	510	567	20	14	494	526	19	9	250	269	20	4	286	263	6	1	407	416	0	12	930	789	5	8	437	471	8	6	188	199	2	6	502	477	5	8	168	135				
28	2	484	408	21	14	806	785	20	9	328	359	21	4	361	386	4	1	1474	1426	6	11	681	672	3	10	1114	1156	6	6	187	165	3	6	1173	1146	1	6	336	371				
30	2	227	225	22	15	668	594	21	9	533	529	22	5	675	654	8	1	331	334	2	12	819	785	9	8	422	395	0	7	346	342	4	6	514	525	2	9	330	338				
32	2	210	244	23	15	249	249	22	9	403	383	23	5	291	281	9	1	572	580	3	12	485	308	4	9	197	184	1	7	472	491	5	6	336	371	4	9	169	137				
34	2	236	241	24	16	249	249	23	9	346	346	24	5	182	134	10	2	818	823	4	12	656	360	5	10	235	245	2	7	807	516	6	6	909	643	4	9	169	137				
36	3	602	547	25	16	561	561	24	9	862	906	25	5	1844	1909	0	2	1783	1781	6	12	285	256	4	9	901	921	4	6	624	630	8	6	428	437	1	10	808	905				
38	3	633	687	26	16	319	285	25	9	827	831	26	5	1219	1278	2	2	1960	1994	1	13	621	626	6	9	352	344	7	7	1047	1033	2	7	815	791	0	11	533	544				
40	3	2004	2008	27	16	246	218	26	9	417	451	27	5	181	131	3	2	668	646	2	13	263	236	7	9	445	436	8	7	302	335	3	7	325	303	1	12	616	619				
42	3	674	648	28	16	648	648	27	9	468	468	28	5	1035	1117	3	3	1034	1071	4	12	656	666	2	11	335	380	9	6	970	929	4	10	489	516	2	10	326	330				
44	3	359	378	29	16	606	560	28	10	628	635	29	5	570	570	6	2	509	461	0	14	229	214	10	10	470	487	1	8	562	547	8	7	744	730	4	0	316	315				
46	3	1348	1314	30	16	1314	1314	29	10	518	518	30	5	638	624	9	2	815	810	2	14	229	214	11	10	470	487	1	8	562	547	8	7	744	730	4	0	316	315				
48	3	968	949	31	16	1034	1034	30	10	1099	1114	31	5	613	619	5	2	1681	1634	5	13	351	333	0	10	743	758	0	8	623	608	1	8	777	747	7	0	256	236				
50	3	474	491	32	16	502	523	31	10	722	735	32	6	436	401	10	2	311	290	0	14	229	214	11	10	470	487	1	8	562	547	8	7	744	730	4	0	316	315				
52	3	613	561	33	16	1236	1210	32	10	655	688	33	6	915	926	11	3	915	926	11	3	915	926	11	3	915	926	11	3	915	926	11	3	915	926	11	3	915	926				
54	3	148	156	34	16	1216	1216	33	10	199	199	34	6	495	465	12	3	364	361	7	0	448	488	12	6	682	682	0	9	672	663	2	9	292	294	1	2	559	524				
56	3	456	508	35	16	748	748	34	10	336	328	35	6	342	361	1	3	574	594	1	0	658	636	1	11	253	216	7	9	418	436	5	6	513	562	3	1	280	267				
58	3	845	807	36	16	1262	1282	35	10	319	317	36	6	953	1038	2	3	777	776	6	0	658	636	1	11	253	216	7	9	418	436	5	6	513	562	3	1	280	267				
60	3	929	908	37	16	980	993	36	10	498	493	37	6	353	333	7	3	924	927	3	0	555	853	1	11	253	216	7	9	418	436	5	6	513	562	3	1	280	267				
62	3	149	116	38	16	837	841	37	10	766	718	38	6	608	594	4	3	1061	1117	5	0	323	351	4	11	297	288	2	9	641	642	0	9	333	391	6	1	768	752				
64	3	278	315	39	16	1559	1559	38	10	483	515	39	6	306	293	5	3	641	617	6	0	144	129	11	6	144	129	11	6	144	129	11	6	144	129	11	6	144	129				
66	3	769	802	40	16	1974	1974	39	10	197	197	40	6	495	465	10	6	364	361	7	0	448	488	12	6	682	682	0	9	672	663	2	9	292	294	1	2	559	524				
68	3	351	318	41	16	376	369	40	11	177	115	41	7	1174	1238	7	3	215	238																								

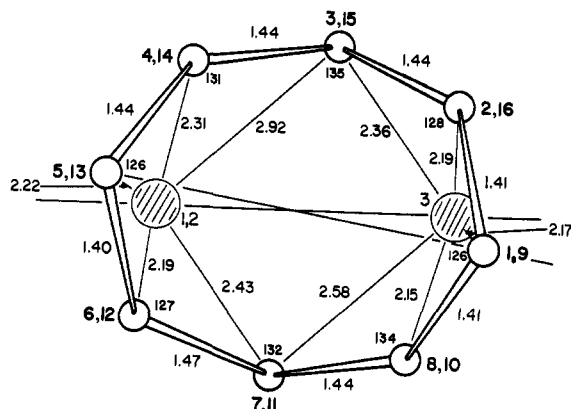


Figure 3. A composite picture of the two  $C_8H_8Ru_2$  moieties, giving mean values of the chemically equivalent bond lengths. For each of the atoms except Ru(3), the use of a pair of numbers, say (1,2), implies either 1 or 2. No superposition of atoms is implied. The numbers given to two decimal places are inter-nuclear distances in Å and the remaining three-digit numbers are C-C-C angles.

### Discussion

The crystal structure of  $(C_8H_8)_2Ru_3(CO)_4$  consists of the packing of discrete molecular units separated by normal intermolecular contact distances. Each mo-

Table II. Final Atomic Positional and Thermal Parameters<sup>a</sup>

Atom	x	y	z	B, Å <sup>2</sup>
Ru <sub>1</sub>	-0.66267 (13)	0.35439 (10)	0.88661 (8)	2.4 <sup>b</sup>
Ru <sub>2</sub>	-0.61212 (14)	0.56985 (10)	0.86235 (9)	3.0 <sup>b</sup>
Ru <sub>3</sub>	-0.89698 (12)	0.49256 (9)	0.84821 (7)	2.0 <sup>b</sup>
C <sub>1</sub>	-1.0242 (17)	0.6327 (14)	0.8718 (11)	3.8 (4)
C <sub>2</sub>	-0.9821 (18)	0.5931 (15)	0.9545 (11)	3.9 (4)
C <sub>3</sub>	-0.8445 (17)	0.5773 (13)	0.9829 (10)	3.2 (3)
C <sub>4</sub>	-0.7198 (19)	0.6371 (16)	0.9848 (12)	4.4 (4)
C <sub>5</sub>	-0.6671 (21)	0.7195 (15)	0.9296 (12)	4.8 (4)
C <sub>6</sub>	-0.6942 (19)	0.7299 (14)	0.8379 (12)	4.1 (4)
C <sub>7</sub>	-0.7947 (18)	0.6672 (14)	0.7856 (12)	3.8 (4)
C <sub>8</sub>	-0.9369 (15)	0.6483 (13)	0.7973 (10)	2.7 (3)
C <sub>9</sub>	-1.0556 (15)	0.3902 (11)	0.7979 (9)	2.3 (3)
C <sub>10</sub>	-1.0199 (17)	0.3568 (15)	0.8817 (11)	3.8 (4)
C <sub>11</sub>	-0.8968 (17)	0.3081 (12)	0.9179 (10)	2.8 (3)
C <sub>12</sub>	-0.8099 (19)	0.2241 (14)	0.8857 (12)	4.2 (4)
C <sub>13</sub>	-0.7446 (19)	0.2210 (15)	0.8070 (12)	4.2 (4)
C <sub>14</sub>	-0.7268 (17)	0.3075 (13)	0.7456 (11)	3.4 (4)
C <sub>15</sub>	-0.8155 (17)	0.3963 (13)	0.7268 (10)	3.1 (3)
C <sub>16</sub>	-0.9631 (18)	0.4112 (14)	0.7307 (11)	3.8 (4)
C <sub>1A</sub>	-0.6338 (16)	0.3854 (12)	1.0013 (10)	3.2 (3)
O <sub>1A</sub>	-0.6174 (13)	0.3986 (10)	1.0771 (8)	5.1 (3)
C <sub>1B</sub>	-0.4836 (16)	0.3203 (12)	0.8749 (11)	2.9 (3)
O <sub>1B</sub>	-0.3654 (14)	0.2961 (11)	0.8726 (9)	5.9 (3)
C <sub>2A</sub>	-0.5430 (20)	0.5229 (15)	0.7582 (13)	4.7 (4)
O <sub>2A</sub>	-0.4890 (15)	0.4983 (12)	0.6895 (9)	6.3 (3)
C <sub>2B</sub>	-0.4774 (21)	0.5628 (16)	0.9135 (13)	5.0 (3)
O <sub>2B</sub>	-0.3323 (18)	0.5570 (13)	0.9471 (11)	7.6 (4)

<sup>a</sup> Numbers in parentheses are estimated standard deviations occurring in the last digits listed. <sup>b</sup> These values of B are the equivalent isotropic thermal parameters corresponding to the anisotropic thermal vibration tensors having the following components ( $\times 10^3$ ).

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ru <sub>1</sub>	599 (14)	387 (9)	265 (6)	46 (10)	-25 (9)	-12 (6)
Ru <sub>2</sub>	848 (17)	476 (10)	302 (7)	-221 (12)	-34 (10)	-4 (7)
Ru <sub>3</sub>	563 (15)	298 (9)	220 (6)	16 (10)	-6 (8)	2 (6)

lecular unit, shown in Figures 1 and 2, is crystallographically asymmetric but has approximate  $C_2$  symmetry with the twofold axis bisecting the Ru<sub>1</sub>-Ru<sub>2</sub> line and passing through Ru<sub>3</sub>.

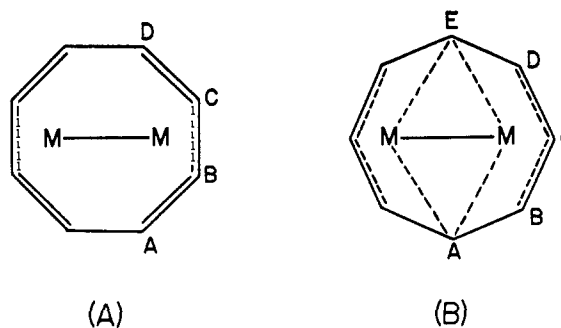


Figure 4. Idealized symmetrical bonding schemes for a  $(C_8H_8)M_2$  system.

The molecular structure may be thought of as derived from that of  $Ru_3(CO)_{12}$  with the  $\pi$ -electron density of the cyclooctatetraene rings replacing that of eight CO groups. The  $Ru_3(CO)_{12}$  molecule<sup>15</sup> is isostructural with

Table III. Intramolecular Distances<sup>a</sup> in  $(COT)_2Ru_3(CO)_4$

Atoms	Distance, Å	Atoms	Distance, Å
Ru <sub>1</sub> -Ru <sub>2</sub>	2.782 (2)	Ru <sub>1</sub> -C <sub>11</sub>	2.40 (2)
Ru <sub>1</sub> -Ru <sub>3</sub>	2.928 (2)	Ru <sub>1</sub> -C <sub>12</sub>	2.18 (2)
Ru <sub>2</sub> -Ru <sub>3</sub>	2.947 (2)	Ru <sub>1</sub> -C <sub>13</sub>	2.22 (2)
		Ru <sub>1</sub> -C <sub>14</sub>	2.32 (2)
		Ru <sub>1</sub> -C <sub>15</sub>	2.91 (2)
C <sub>1</sub> -C <sub>2</sub>	1.42 (2)	Ru <sub>2</sub> -C <sub>3</sub>	2.92 (2)
C <sub>2</sub> -C <sub>3</sub>	1.42 (2)	Ru <sub>2</sub> -C <sub>4</sub>	2.30 (2)
C <sub>3</sub> -C <sub>4</sub>	1.43 (2)	Ru <sub>2</sub> -C <sub>5</sub>	2.21 (2)
C <sub>4</sub> -C <sub>5</sub>	1.43 (3)	Ru <sub>2</sub> -C <sub>6</sub>	2.20 (2)
C <sub>5</sub> -C <sub>6</sub>	1.43 (3)	Ru <sub>2</sub> -C <sub>7</sub>	2.46 (2)
C <sub>6</sub> -C <sub>7</sub>	1.49 (3)		
C <sub>7</sub> -C <sub>8</sub>	1.42 (2)	Ru <sub>3</sub> -C <sub>8</sub>	2.37 (2)
C <sub>8</sub> -C <sub>1</sub>	1.43 (2)	Ru <sub>3</sub> -C <sub>2</sub>	2.22 (2)
		Ru <sub>3</sub> -C <sub>1</sub>	2.19 (2)
C <sub>9</sub> -C <sub>10</sub>	1.39 (2)	Ru <sub>3</sub> -C <sub>3</sub>	2.14 (2)
C <sub>10</sub> -C <sub>11</sub>	1.45 (2)	Ru <sub>3</sub> -C <sub>4</sub>	2.60 (2)
C <sub>11</sub> -C <sub>12</sub>	1.44 (2)		
C <sub>12</sub> -C <sub>13</sub>	1.36 (2)	Ru <sub>3</sub> -C <sub>15</sub>	2.35 (2)
C <sub>13</sub> -C <sub>14</sub>	1.45 (3)	Ru <sub>3</sub> -C <sub>16</sub>	2.16 (2)
C <sub>14</sub> -C <sub>15</sub>	1.44 (2)	Ru <sub>3</sub> -C <sub>9</sub>	2.15 (2)
C <sub>15</sub> -C <sub>17</sub>	1.45 (2)	Ru <sub>3</sub> -C <sub>10</sub>	2.15 (2)
C <sub>16</sub> -C <sub>9</sub>	1.39 (2)	Ru <sub>3</sub> -C <sub>11</sub>	2.56 (2)
		C <sub>1A</sub> -O <sub>1A</sub>	1.18 (2)
Ru <sub>1</sub> -C <sub>1A</sub>	1.82 (2)	C <sub>1B</sub> -O <sub>1B</sub>	1.19 (2)
Ru <sub>1</sub> -C <sub>1B</sub>	1.80 (2)	C <sub>2A</sub> -O <sub>2A</sub>	1.21 (2)
Ru <sub>2</sub> -C <sub>2A</sub>	1.83 (2)	C <sub>2B</sub> -O <sub>2B</sub>	1.23 (3)
Ru <sub>2</sub> -C <sub>2B</sub>	1.79 (2)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations occurring in the last digit listed.

$Os_3(CO)_{12}$ <sup>16</sup> and has Ru-Ru distances of 2.855, 2.844, and 2.851 Å. In the present instance, the metal-metal bond distances (Ru<sub>1</sub>-Ru<sub>2</sub> = 2.782 (2) Å, Ru<sub>1</sub>-Ru<sub>3</sub> = 2.928 (2) Å, and Ru<sub>2</sub>-Ru<sub>3</sub> = 2.947 (2) Å)<sup>c</sup> reflect both in magnitude and variation the inferior ability of  $C_8H_8$  in comparison with CO to remove  $\pi$ -antibonding electrons from the triangular metal atom cluster. Thus, the Ru-Ru bonds involving the Ru atom which has no CO groups are the longer ones.

The most important and interesting features of the molecular structure have to do with the mode of attachment of the  $C_8H_8$  rings to the  $Ru_3$  cluster, particularly because the rings execute some reorientation (presumably an internal rotation) so rapidly in solution at room

(15) E. R. Corey and L. F. Dahl, submitted for publication.

(16) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1, 521 (1962).

Table IV. Intramolecular Angles<sup>a</sup> in (COT)<sub>2</sub>Ru<sub>3</sub>(CO)<sub>4</sub>

Atoms	Angle, deg	Atoms	Angle, deg
Ru <sub>1</sub> -Ru <sub>2</sub> -Ru <sub>3</sub>	61.39 (4)	C <sub>11</sub> -Ru <sub>1</sub> -C <sub>12</sub>	36.3 (6)
Ru <sub>2</sub> -Ru <sub>1</sub> -Ru <sub>3</sub>	62.09 (4)	C <sub>12</sub> -Ru <sub>1</sub> -C <sub>13</sub>	36.0 (7)
Ru <sub>1</sub> -Ru <sub>3</sub> -Ru <sub>2</sub>	56.52 (4)	C <sub>13</sub> -Ru <sub>1</sub> -C <sub>14</sub>	37.1 (6)
		C <sub>14</sub> -Ru <sub>1</sub> -C <sub>15</sub>	29.4 (5)
		C <sub>11</sub> -Ru <sub>1</sub> -C <sub>15</sub>	74.1 (5)
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	126 (1.5)		
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	137 (1.6)	C <sub>3</sub> -Ru <sub>2</sub> -C <sub>4</sub>	28.8 (6)
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	132 (1.7)	C <sub>4</sub> -Ru <sub>2</sub> -C <sub>5</sub>	36.9 (7)
C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	125 (1.7)	C <sub>5</sub> -Ru <sub>2</sub> -C <sub>6</sub>	37.9 (7)
C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	127 (1.7)	C <sub>6</sub> -Ru <sub>2</sub> -C <sub>7</sub>	36.8 (6)
C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	132 (1.6)	C <sub>7</sub> -Ru <sub>2</sub> -C <sub>8</sub>	74.0 (5)
C <sub>7</sub> -C <sub>8</sub> -C <sub>1</sub>	135 (1.6)		
C <sub>8</sub> -C <sub>1</sub> -C <sub>2</sub>	126 (1.5)		
		C <sub>3</sub> -Ru <sub>3</sub> -C <sub>2</sub>	35.9 (6)
C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub>	133 (1.5)	C <sub>2</sub> -Ru <sub>3</sub> -C <sub>1</sub>	37.6 (6)
C <sub>10</sub> -C <sub>11</sub> -C <sub>12</sub>	132 (1.5)	C <sub>1</sub> -Ru <sub>3</sub> -C <sub>8</sub>	38.6 (6)
C <sub>11</sub> -C <sub>12</sub> -C <sub>13</sub>	127 (1.7)	C <sub>8</sub> -Ru <sub>3</sub> -C <sub>7</sub>	33.0 (6)
C <sub>12</sub> -C <sub>13</sub> -C <sub>14</sub>	127 (1.7)	C <sub>7</sub> -Ru <sub>3</sub> -C <sub>3</sub>	81.7 (6)
C <sub>13</sub> -C <sub>14</sub> -C <sub>15</sub>	130 (1.6)		
C <sub>14</sub> -C <sub>15</sub> -C <sub>16</sub>	133 (1.5)	C <sub>11</sub> -Ru <sub>3</sub> -C <sub>10</sub>	34.7 (6)
C <sub>15</sub> -C <sub>16</sub> -C <sub>9</sub>	130 (1.6)	C <sub>10</sub> -Ru <sub>3</sub> -C <sub>9</sub>	37.8 (6)
C <sub>16</sub> -C <sub>9</sub> -C <sub>10</sub>	125 (1.5)	C <sub>9</sub> -Ru <sub>3</sub> -C <sub>16</sub>	37.6 (6)
		C <sub>16</sub> -Ru <sub>3</sub> -C <sub>15</sub>	37.2 (6)
		C <sub>11</sub> -Ru <sub>3</sub> -C <sub>15</sub>	81.9 (5)
O <sub>1A</sub> -C <sub>1A</sub> -Ru <sub>1</sub>	176 (1.4)	C <sub>1A</sub> -Ru <sub>1</sub> -C <sub>1B</sub>	89.8 (7)
O <sub>1B</sub> -C <sub>1B</sub> -Ru <sub>1</sub>	176 (1.4)	C <sub>1A</sub> -Ru <sub>1</sub> -Ru <sub>2</sub>	83.8 (5)
O <sub>2B</sub> -C <sub>2B</sub> -Ru <sub>2</sub>	179 (1.8)	C <sub>1B</sub> -Ru <sub>1</sub> -Ru <sub>2</sub>	92.8 (5)
O <sub>2A</sub> -C <sub>2A</sub> -Ru <sub>2</sub>	175 (1.7)	C <sub>2A</sub> -Ru <sub>2</sub> -C <sub>2B</sub>	91.9 (9)
		C <sub>2A</sub> -Ru <sub>2</sub> -Ru <sub>1</sub>	82.3 (6)
		C <sub>2B</sub> -Ru <sub>2</sub> -Ru <sub>1</sub>	93.0 (6)

<sup>a</sup> Numbers in parentheses are estimated standard deviations occurring in the last digit listed.

temperature that only one signal is observed for all 16 protons in the molecule. This ring-to-metal bonding can be conveniently discussed in comparison with the two symmetrical arrangements shown schematically in Figure 4.

The arrangement shown in Figure 4A involves a pair of (1,3-diene)-metal interactions. While this exact situation has not as yet been observed in a molecule with a metal-metal bond, it has been seen,<sup>17</sup> for example, in the solid-state configurations of (COT)Fe(CO)<sub>3</sub> and (COT)Fe<sub>2</sub>(CO)<sub>6</sub>. The relevant (C<sub>4</sub>H<sub>4</sub>)Fe(CO)<sub>3</sub> residues have the same geometry in both molecules and pertinent average dimensions are M-A = M-D = 2.14 Å, M-B = M-C = 2.06 Å, A-B = C-D = 1.44 Å, B-C = 1.40 Å, and ∠B = ∠C = 120°, ∠A = ∠D = 130°.

The other mode of ring attachment involves the ring-metal orientation shown in Figure 4B. In such a complex the bonding can be crudely formulated as follows. Each metal atom is bound to three ring carbon atoms in a kind of (π-allyl)metal complex, thereby leaving two carbon atoms of the ring (designated as A and E) each with a half-occupied orbital. After allowance for metal-metal and metal-CO bonds, each metal atom also has a half-occupied orbital remaining in its valence shell. Consequently, four atoms (M, M, A, and E), four orbitals, and four electrons combine to produce a four-center, four-electron delocalized bonding system. This type of bonding has been invoked to account for the molecular structure of (COT)Fe<sub>2</sub>(CO)<sub>6</sub><sup>18</sup> and (TMCOT)Fe<sub>2</sub>(CO)<sub>6</sub>,<sup>19</sup> where TMCOT represents

(17) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4062 (1961); *J. Chem. Phys.*, **37**, 2084 (1962).

(18) E. B. Fleisher, A. L. Stone, R. B. K. Dewar, J. E. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 3158 (1966).

1,3,5,7-tetramethylcyclooctatetraene. The pertinent average geometrical features of these structures are M-B ≈ M-C ≈ M-D ≈ 2.12 Å, M-E ≈ M-A ≈ 2.50 Å, B-C ≈ C-D ≈ 1.38 Å, A-B ≈ D-E ≈ 1.45 Å, and ∠C = 127°.

Both of the molecules for which a structure of type 4B has been found are fluxional; there is time-average equivalence of all ring protons. It seems entirely reasonable to suppose that the rearrangement pathway by which the ring passes from one to another of the equivalent configurations of type 4B carries it through structures of type 4A. Since the rearrangement processes are rapid, it follows that structure 4A must be only a little less stable (perhaps 5–15 kcal/mole) than 4B.

To facilitate discussion of the ring-to-metal interactions in (C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>Ru<sub>3</sub>(CO)<sub>4</sub>, we show in Figure 3 a composite picture of the two crystallographically independent (C<sub>8</sub>H<sub>8</sub>)Ru<sub>2</sub> moieties, which would be rigorously equivalent under strict C<sub>2</sub> symmetry. The view given is a projection of each ring upon a plane perpendicular to a line joining the midpoint of the Ru-Ru axis with the midpoint of the C<sub>3</sub>-C<sub>7</sub> or C<sub>11</sub>-C<sub>15</sub> axes. The distances shown are the averages of corresponding distances in the two separate (C<sub>8</sub>H<sub>8</sub>)Ru<sub>2</sub> portions of the molecule.

It is clear from Figure 3 that the configuration in this compound is neither 4A nor 4B but is approximately halfway between the two. The rotation of the M-M line about its perpendicular bisector which would convert orientation 4A into orientation 4B, assuming the ring to remain fixed, is 22.5°. In fact, the Ru-Ru line is rotated 9.5° away from orientation 4B. Moreover, the C-C distances in the rings do not differ from one another significantly, as Figure 3 shows. The ring conformation is also intermediate, but distinctly closer to what one might expect for structure 4A. Thus the ring fragments (4,14), (5,13), (6,12), (7,11) and (8,10), (1,9), (2,16), (3,15) are each essentially planar, whereas the five-carbon sequences from (3,15) to (7,11) inclusive in either direction are noticeably kinked.

The fact that the (C<sub>8</sub>H<sub>8</sub>)M<sub>2</sub> configuration is intermediate between 4A and 4B makes it difficult to give any simple description of the bonding, and we shall not attempt to rationalize the structure in this way. Instead, it seems more interesting and enlightening to note that, since structures 4A and 4B presumably do not differ very much in stability, one of them (4A) probably corresponding to the activated complex for interchange among the several equivalent forms of the other (4B), the configurations lying between 4A and 4B must also be easily accessible.<sup>20</sup> It may be that only under the influence of intermolecular forces in the crystal does the observed configuration become fixed, whereas in solution configuration 4B (or, less likely, 4A) is adopted as the instantaneous structure. Because of the overall low symmetry, this will be a difficult point to establish, however, even if a limiting low-temperature solution nmr spectrum can be obtained.

With regard to the carbonyl portion of the molecule, we note that the structure found is entirely consistent with the observed infrared spectrum in the CO stretch-

(19) F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 2026 (1968).

(20) Fluxional molecules should, naturally and in general, be the most easily distortable molecules, in a sense or direction corresponding to the pathway of their intramolecular rearrangement.

ing region. Four bands were observed, one of which is very weak. For the  $\text{Ru}_2(\text{CO})_4$  group found, with  $\text{C}_2$  symmetry, four infrared-active CO stretching modes would be expected. One of these would likely be essentially the antisymmetrically coupled stretching of the two CO groups (1A and 2A) which are approximately perpendicular to the plane of the  $\text{Ru}_3$  triangle. This mode would have only a slight dipolar transition moment, thus accounting for the one extremely weak band.

Lastly, it may be noted that the  $(\text{C}_5\text{H}_5)_2\text{Ru}_3(\text{CO})_4$  molecule is dissymmetric in its idealized  $\text{C}_2$  symmetry. Since it crystallizes in enantiomeric crystals, it would perhaps be feasible to study the rate of racemization, or at least to set a lower limit on it, by preparing solutions from individual single crystals. Racemization may well be a very rapid process, since it could readily be accomplished in the following way. The CO(1A)

and CO(2A) groups could swing toward the center of the Ru(1)–Ru(2) bond and become bridging CO groups. This sort of interconversion of terminal with bridging systems is well known, for example, in  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,<sup>21</sup>  $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ ,<sup>21</sup> and  $\text{Co}_2(\text{CO})_8$ .<sup>22</sup> If, at the same time as the bridges form, the  $\text{C}_5\text{H}_5$  rings move slightly so that the plane of the  $\text{Ru}_3$  triangle becomes a bisector of the mean plane of each ring, an intermediate without chirality will be formed, which may then return to either enantiomer of the chiral structure with equal probability, thereby accomplishing racemization. Thus, a study of the rate of racemization of the  $(\text{C}_5\text{H}_5)_2\text{Ru}_3(\text{CO})_4$  molecule would be equivalent to a study of the rate of interconversion of the bridged and nonbridged  $\text{Ru}_2(\text{CO})_4$  systems, and would therefore be of fundamental interest.

- (21) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).  
 (22) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).

## Transition Metal Carbonyl Anions. I. The Course of the Reduction of Chromium Hexacarbonyl<sup>1</sup>

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**Abstract:** In order to reveal the chemical and physical properties of group VI transition metal carbonyl anions, a study of the chromium hexacarbonyl reduction has been undertaken. Chromium hexacarbonyl was reduced in tetrahydrofuran and hexamethylphosphoramide with sodium, potassium, and cesium amalgam, phenanthrene-sodium, and trimesitylboron sodium. An extensive comparison of infrared spectra suggests the formation of  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ ,  $[\text{Cr}(\text{CO})_5]^{2-}$ ,  $[\text{Cr}(\text{CO})_5\text{HMPT}]^{2-}$ , and  $[\text{Cr}_2(\text{CO})_9]^{4-}$  ions. The conditions for isolation and purification of the ions are discussed.

The carbonylmetallate ions of group VI<sup>2</sup> transition metal elements and their organometallic derivatives are potentially useful in the synthesis of metal-metal and metal-metalloid bonds.<sup>3</sup> With a combination of suitable ligands these materials are intriguing starting points toward the synthesis of catenated transition metal compounds, or "synthetic metals" as they might be called. These, in turn, offer the possibility of studying solid-state physical and chemical properties such as magnetic behavior and heterogeneous catalysis.

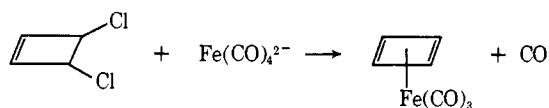
In other instances, the carbonylmetallate ions may be valuable in the preparation of organometallic compounds. Such a case in particular has been the eminently successful role of these ions in the synthesis of cyclobutadiene-metal carbonyl complexes.<sup>4</sup>

(1) Presented in part at the Third International Organometallic Symposium at Munich, Germany, Aug 29–Sept 1, 1967.

(2) (a) R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964); (b) F. Calderazzo, R. Ercoli, and G. Natta, "Organic Synthesis Via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 150.

(3) (a) R. E. Dessy, and P. M. Weissman, *J. Am. Chem. Soc.*, **88**, 5124 (1966); (b) U. Anders and W. A. G. Graham, *ibid.*, **89**, 539 (1967); (c) J. K. Ruff, *Inorg. Chem.*, **6**, 2080 (1967).

(4) R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Commun.*, 1208 (1967).



From another aspect the anions are of interest because they are isoelectronic with known metal carbonyls. For example,  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ <sup>5</sup> is isoelectronic with  $\text{Mn}_2(\text{CO})_{10}$ ;  $[\text{Cr}(\text{CO})_5]^{2-}$  is related to the unstable species  $\text{Mn}(\text{CO})_5$  and to the known  $\text{Fe}(\text{CO})_5$  molecule. Other ions such as  $[\text{Cr}_2(\text{CO})_9]^{2-}$  and  $[\text{Re}_2(\text{CO})_9]^{-6,7}$  are related and  $[\text{Cr}_2(\text{CO})_9]^{4-}$  is isoelectronic with  $\text{Fe}_2(\text{CO})_9$ .

Behrens and his coworkers<sup>8–11</sup> have reported no less than five different carbonylmetallate ions of group VI from various synthetic routes. Some of these ions are  $[\text{Cr}(\text{CO})_5]^{2-}$ ,  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ ,  $[\text{Mo}_2(\text{CO})_9]^{4-}$ ,  $[\text{Cr}_3(\text{CO})_{14}]^{2-}$ , and  $[\text{Cr}_2\text{H}(\text{CO})_{10}]^-$ .

(5) R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).

(6) G. W. Parshall, *ibid.*, **86**, 361 (1964).

(7) R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 69 (1966).

(8) H. Behrens and R. Weber, *Z. Anorg. Allgem. Chem.*, **291**, 123 (1957).

(9) H. Behrens and J. Vogl, *Chem. Ber.*, **96**, 2220 (1963).

(10) H. Behrens and W. Haag, *ibid.*, **94**, 312 (1961).

(11) H. Behrens and W. Haag, *ibid.*, **94**, 320 (1961).