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Molecular Structure and Bonding in Diethylenetriaminechromium Tricarbonyl: The Cr(0) and Approximate Mn(0) Radii[1]

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Received January 31, 1966

The crystal and molecular structure of *cis*-Cr(dien)$(CO)_3$ (dien = diethylenetriamine) has been determined by single crystal X-ray diffraction studies. The molecular structure is derived, as expected, from that of octahedral $Cr(CO)_6$, the substituents being mutually *cis*. The compound is crystallographically isostructural with its Mo analog, whose structure was recently reported. From the Cr–N bond lengths a single-bond radius of 1.48 ± 0.01 A is obtained for Cr(0) in $Cr(CO)_6$ and its derivatives. It is also inferred that the single-bond radius for Mn in derivatives of $Mn_2(CO)_{10}$ is probably about 1.39 A, with 1.43 A being a fairly certain upper limit. Comparison of the Cr–CO bond lengths in Cr(dien)$(CO)_3$ with those in Cr(arene)$(CO)_3$ compounds implies that the arene rings show little if any π acidity toward the $Cr(CO)_3$ moiety in the ground states of these arene derivatives.

Introduction

Recently there has been considerable interest in this laboratory[3-6] and elsewhere[7-9] in the detailed description of the bonding of ligands to the metal atoms in very low (or zero) formal oxidation states in metal carbonyls and their derivatives. Both structural and spectroscopic observations are valuable in attempting to elucidate the problem. From the purely structural point of view, it is necessary to know general structures of the molecules, that is connexity of bonds and molecular symmetry, as well as accurate values of bond distances, from which such elusive quasi-experimental, quasi-theoretical parameters as metal single bond radii and metal–ligand bond orders can be deduced.

The present paper reports a structural study of an amine-substituted derivative of chromium carbonyl, from which information and conclusions pertinent to the question of Cr–CO bonding may be obtained.

Experimental Section

Preparation of *cis*-(Diethylenetriamine)chromium Tricarbonyl.—The Cr(dien)$(CO)_3$ was prepared by heating at 150° for 0.5 hr chromium hexacarbonyl, 1.5 g, with an excess of diethylenetriamine, 5 ml, under an atmosphere of nitrogen.[3b,10] Slow cooling of the reaction mixture to room temperature allowed the formation of crystals suitable for X-ray work. The orange-brown rhombohedral crystals were washed with ethanol, then pentane, and dried in a vacuum desiccator.

X-Ray Crystallographic Study.—The rhombohedra were found to belong to the orthorhombic system with cell dimensions a = 8.312 ± 0.002, b = 11.81 ± 0.02, c = 10.05 ± 0.01 A. The compound just floats in iodobutane of density 1.62. Assuming the density of the crystals to be 1.60 and using the molecular weight of 239 amu the number of molecules per unit cell was calculated to be 3.98. The systematic absences $h00$ for $h \neq 2n$, $0k0$ for $k \neq 2n$, $00l$ for $l \neq 2n$ observed on precession photographs uniquely determined the space group as $P2_12_12_1$.

The intensities of about 1530 reflections, $0 < 2\theta \leq 58°$, were collected using the General Electric XRD-5 X-ray diffractometer equipped with a Furnas–Harker eucentric goniometer and a scintillation counter, with Mo Kα radiation. The crystal, of approximate dimensions 0.4 mm on an edge, was mounted in a nitrogen-filled capillary with the c axis vertical and parallel to the spindle. The intensities were measured using a modification of the moving crystal–moving counter method of Furnas.[11] Lorentz-polarization corrections were applied but absorption was neglected (μ = 12 cm^{-1}).

Solution and Refinement of Structure.—A three-dimensional Patterson synthesis was computed[12] using all reflections. From the large peak in each of the Harker sections ($^1/_2$, y, z), (x, $^1/_2$, z), (x, y, $^1/_2$), the fractional coordinates of the chromium atom were estimated to be x = 0.318, y = 0.396, z = 0.811.

A Fourier summation was computed[12] with all phases the same as those given by the chromium atoms, and this gave a fairly clear picture of the entire molecule. Two cycles of least-squares refinement[13] of the over-all scale factor and Cr, C, O, and N atom coordinates produced a residual[14] of 0.17. Four cycles of refinement of the atom coordinates and the isotropic temperature factors lowered the residual to 0.13. A Fourier electron density map computed at this time clearly showed this compound to be isostructural with Mo(dien)$(CO)_3$.[5] An error analysis, dividing the reflections into groups of 50 by relative intensity, showed nothing unusual, and it was decided best to give all reflections equal weights.

Refining the scale factor and one of the bridging carbon atoms, C_4, reduced the residual to 0.12. A difference Fourier at this stage indicated a need for anisotropic temperature factors and showed electron density in the regions where the hydrogen atoms would be expected. Working from a model and modifying the values to best fit the Fourier map the coordinates of the hydrogen atoms were estimated. Two cycles of varying only the hydrogen atom coordinates and isotropic temperature factors slightly raised the residual and only a few of the hydrogen atom positions remained reasonable. The hydrogen atoms were therefore dropped from consideration.

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[1] Supported by grants from the United States Atomic Energy Commission and the National Science Foundation.

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[12] All Patterson and Fourier summations were computed using the ERFR2 Fourier summation program for the IBM 709/7090 computer written by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, 1962.

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[14] Defined as $[\Sigma w||F_o| - |F_c||]/\Sigma|wF_o|$.

TABLE I

CALCULATED, F_c, AND OBSERVED, $|F_o|$, STRUCTURE FACTORS

H	K	FOBS	FCAL
****L = 0******			
2	0	1033	1116
4	0	185	115
6	0	721	662
8	0	2224	2204
10	0	894	849
1	1	4105	5020
2	1	172	214
3	1	3059	3104
4	1	2313	2314
5	1	1941	1799
6	1	2638	2586
7	1	1273	1238
8	1	982	920
9	1	881	895
10	1	283	342
11	1	853	936
0	2	1067	1028
1	2	212	716
2	2	1787	1798
3	2	185	370
4	2	1208	1070
5	2	2367	2256
6	2	89	90
7	2	990	905
8	2	667	705
9	2	685	684
10	2	186	169
11	2	758	774
1	3	2195	2341
2	3	472	440
3	3	1008	971
4	3	2001	1899
5	3	1100	1046
6	3	1902	1842
7	3	50	54
8	3	749	780
9	3	821	818
10	3	44	41
11	3	385	408
0	4	7186	7999
1	4	5214	5245
2	4	1579	1318
3	4	1159	1009
4	4	323	416
5	4	626	601
6	4	1067	988
7	4	752	708
8	4	1309	1312
9	4	418	422
10	4	665	702
11	4	203	176
1	5	5124	5150
2	5	778	702
3	5	1429	1563
4	5	193	232
5	5	775	761
6	5	1331	1282
7	5	1759	1668
8	5	224	156
9	5	860	879
10	5	308	393
0	6	2612	2383
1	6	977	895
2	6	835	811
3	6	2770	2709
4	6	297	327
5	6	3003	2952
6	6	769	816
7	6	644	534
8	6	913	917
9	6	301	289
10	6	292	249
1	7	2659	2561
2	7	2191	2086
3	7	644	555
4	7	1981	1867
5	7	770	729
6	7	2087	2051
7	7	482	470
8	7	41	22
9	7	573	557
10	7	340	348
0	8	1974	1730
1	8	2267	2064
2	8	1511	1432
3	8	1510	1581
4	8	549	576
5	8	1232	1162
6	8	693	707
7	8	768	778
8	8	529	532
9	8	249	157
1	9	2218	1814
2	9	1717	1774
3	9	784	727
4	9	487	457
5	9	37	7
6	9	389	377
7	9	979	934
8	9	44	23
9	9	757	792
0	10	1027	870
1	10	419	329
2	10	822	816
3	10	868	843
4	10	594	641
5	10	638	651
6	10	1071	1063
7	10	331	312
8	10	789	862
1	11	460	401
2	11	1784	1811
3	11	360	316
4	11	1613	1643
5	11	41	58
6	11	745	736
7	11	485	572
8	11	149	175
0	12	801	792
1	12	758	780
2	12	1058	1079
3	12	1450	1474
4	12	235	156
5	12	936	951
6	12	363	348
7	12	407	396
1	13	870	896
2	13	682	682
3	13	642	657
4	13	174	274
5	13	337	335
6	13	489	520
0	14	800	853
1	14	184	245
2	14	736	770
3	14	63	157
4	14	393	366
5	14	132	68
1	15	402	470
2	15	473	534
3	15	443	446
4	15	640	721
0	16	277	244
1	16	394	479
****L = 1******			
1	0	1626	1958
2	0	2372	2219
3	0	5040	5229
4	0	1519	1455
5	0	4791	4944
6	0	1199	1193
7	0	1719	1556
8	0	291	211
9	0	422	378
10	0	315	136
11	0	789	817
0	1	1465	1335
1	1	4290	4679
2	1	2815	2658
3	1	1377	1324
4	1	2795	2876
5	1	1867	1792
6	1	2945	2879
7	1	637	622
8	1	641	656
9	1	673	625
10	1	185	182
11	1	380	361
0	2	5909	6605
1	2	2871	2661
2	2	2296	1983
3	2	740	757
4	2	728	459
5	2	322	343
6	2	1032	1024
7	2	620	582
8	2	1214	1244
9	2	352	299
10	2	494	531
11	2	333	229
0	3	3439	3161
1	3	1353	1234
2	3	1001	859
3	3	1160	1072
4	3	658	608
5	3	989	971
6	3	1592	1573
7	3	1218	1118
8	3	494	452
9	3	613	692
10	3	452	443
11	3	445	457
0	4	4585	4221
1	4	137	89
2	4	831	787
3	4	2769	2903
4	4	1723	1620
5	4	2837	2733
6	4	1118	1147
7	4	1066	974
8	4	736	680
9	4	196	181
10	4	127	115
0	5	2332	1654
1	5	2636	2466
2	5	3360	3206
3	5	602	541
4	5	2658	2588
5	5	652	637
6	5	2352	2254
7	5	534	567
8	5	377	389
9	5	613	608
10	5	442	419
0	6	4568	4259
1	6	1668	1482
2	6	2190	2218
3	6	951	821
4	6	870	865
5	6	914	837
6	6	1167	1076
7	6	604	562
8	6	963	968
9	6	331	330
10	6	605	638
0	7	2193	2121
1	7	3030	2953
2	7	597	551
3	7	657	625
4	7	1329	1315
5	7	555	593
6	7	598	570
7	7	1282	1228
8	7	564	589
9	7	1071	1117
10	7	443	429
0	8	1800	1737
1	8	769	644
2	8	1786	1676
3	8	1557	1503
4	8	1288	1235
5	8	1431	1343
6	8	946	940
7	8	644	712
8	8	787	782
9	8	223	191
0	9	975	1002
1	9	1446	1301
2	9	1535	1438
3	9	627	613
4	9	1118	1085
5	9	680	623
6	9	888	917
7	9	767	762
8	9	360	306
9	9	219	217
0	10	847	723
1	10	899	819
2	10	835	810
3	10	1399	1446
4	10	479	475
5	10	702	695
6	10	219	229
7	10	204	241
8	10	394	408
0	11	528	606
1	11	1812	1806
2	11	663	693
3	11	893	928
4	11	364	382
5	11	661	682
6	11	385	402
7	11	907	947
8	11	360	346
0	12	1304	1372
1	12	673	677
2	12	1010	1050
3	12	1031	1048
4	12	264	255
5	12	620	624
6	12	738	765
7	12	603	623
0	13	411	406
1	13	613	601
2	13	620	578
3	13	552	576
4	13	1013	1081
5	13	393	397
6	13	467	485
0	14	252	39
1	14	275	312
2	14	444	519
3	14	810	839
4	14	214	128
5	14	506	534
0	15	232	102
1	15	569	636
2	15	530	652
3	15	517	577
4	15	438	525
0	16	708	844
1	16	383	415
****L = 2******			
0	0	5260	6417
1	0	3299	3548
2	0	4471	4893
3	0	1275	1227
4	0	1443	1208
5	0	375	422
6	0	2146	2111
7	0	1620	1604
8	0	1487	1391
9	0	1257	1312
10	0	656	676
11	0	305	317
0	1	3106	2906
1	1	3611	3980
2	1	4512	4573
3	1	2342	2176
4	1	1215	1296
5	1	613	554
6	1	1445	1284
7	1	964	982
8	1	850	817
9	1	1010	1057
10	1	585	634
11	1	472	489
0	2	390	407
1	2	2965	2825
2	2	2511	2369
3	2	2527	2251
4	2	877	857
5	2	1470	1512
6	2	1207	1204
7	2	173	176
8	2	54	8
9	2	254	224
10	2	360	386
11	2	557	596
0	3	4240	4175
1	3	986	1063
2	3	2205	2145
3	3	1790	1666
4	3	869	746
5	3	1630	1631
6	3	1376	1340
7	3	386	416
8	3	695	691
9	3	521	525
10	3	296	341
11	3	364	350
0	4	3219	2866
1	4	2664	2482
2	4	2734	2467
3	4	1904	1950
4	4	657	684
5	4	1326	1349
6	4	1186	1104
7	4	868	887
8	4	1010	973
9	4	747	735
10	4	643	626
0	5	1991	1907
1	5	3820	3534
2	5	1531	1383
3	5	893	857
4	5	706	715
5	5	808	870
6	5	1082	1049
7	5	1112	1031
8	5	1048	1025
9	5	1029	1033
10	5	494	521
0	6	176	349
1	6	1236	1299
2	6	1402	1264
3	6	2502	2407
4	6	1755	1745
5	6	1483	1366
6	6	1069	1026
7	6	836	796
8	6	398	359
9	6	277	246
10	6	316	305
0	7	1149	1115
1	7	2234	2236
2	7	1827	1724
3	7	1774	1690
4	7	1715	1577
5	7	1428	1359
6	7	1237	1189
7	7	924	900
8	7	481	411
9	7	142	175
10	7	308	296
0	8	1518	1377
1	8	1266	1193
2	8	955	856
3	8	1746	1671
4	8	1577	1531
5	8	1218	1205
6	8	751	703
7	8	796	806
8	8	661	715
9	8	338	295
0	9	1640	1505
1	9	1318	1125
2	9	894	840
3	9	876	871
4	9	345	384
5	9	598	627
6	9	652	660
7	9	406	447
8	9	521	632
9	9	690	691
0	10	1078	1074
1	10	720	761
2	10	753	754
3	10	618	550
4	10	452	426
5	10	429	407
6	10	691	664
7	10	641	699
8	10	529	520
0	11	262	414
1	11	731	675
2	11	965	886
3	11	706	741
4	11	1389	1435
5	11	938	1009
6	11	638	674
7	11	374	325
8	11	134	73
0	12	1010	1074
1	12	685	915
2	12	914	965
3	12	1142	1174
4	12	776	764
5	12	805	805
6	12	694	713
7	12	371	461
0	13	681	655
1	13	768	811
2	13	708	775
3	13	598	606
4	13	449	487
5	13	401	446
6	13	465	494
0	14	608	634
1	14	514	557
2	14	509	567
3	14	45	46
4	14	159	103
5	14	66	57
0	15	615	636
1	15	450	479
2	15	341	320
3	15	377	466
****L = 3******			
1	0	1518	1344
2	0	6297	6799
3	0	4087	4010
4	0	2492	2564
5	0	1281	1237
6	0	1518	1419
7	0	310	275
8	0	902	945
9	0	83	54
10	0	732	720
11	0	547	472
0	1	1912	1597
1	1	538	637
2	1	2901	2839
3	1	4267	4277
4	1	1049	954
5	1	2325	2312
6	1	1663	1649
7	1	1001	991
8	1	1214	1130
9	1	527	599
10	1	218	302
11	1	481	475
0	2	801	607
1	2	3025	2829
2	2	1435	1415
3	2	1616	1490
4	2	977	884
5	2	628	576
6	2	932	879
7	2	1062	1068
8	2	663	713
9	2	1136	1148
10	2	380	321
11	2	135	51
0	3	1548	978
1	3	1920	1870
2	3	3168	3168
3	3	2045	1910
4	3	1033	1022
5	3	647	646
6	3	1276	1158
7	3	429	392
8	3	775	814
9	3	668	645
10	3	554	569
0	4	1154	1056
1	4	1845	1625
2	4	2944	2837
3	4	2053	1935
4	4	2297	2276
5	4	795	766
6	4	1190	1128
7	4	629	703
8	4	530	501
9	4	615	606
10	4	439	417
0	5	1187	1239
1	5	810	743
2	5	1849	1768
3	5	3036	2904
4	5	1656	1573
5	5	1805	1725
6	5	641	626
7	5	497	520
8	5	760	827
9	5	230	245
10	5	321	310
0	6	1739	1602
1	6	1658	1547
2	6	1141	1022
3	6	1927	1869
4	6	1127	1090
5	6	741	670
6	6	756	721
7	6	1133	1426
8	6	941	946
9	6	735	739
10	6	516	533
0	7	2586	2457
1	7	2069	2013
2	7	2735	2675
3	7	1742	1767
4	7	639	654
5	7	712	733
6	7	806	738
7	7	284	282
8	7	982	952
9	7	612	628
0	8	1639	1680
1	8	2176	2083
2	8	1222	1205
3	8	1090	979
4	8	1444	1355
5	8	462	380
6	8	610	585
7	8	538	523
8	8	417	441
9	8	711	741
0	9	549	610
1	9	1074	1012
2	9	766	775
3	9	987	927
4	9	955	899
5	9	1177	1274
6	9	485	476
7	9	477	482
8	9	110	3
9	9	431	347
0	10	35	141
1	10	446	400
2	10	231	306
3	10	728	690
4	10	1101	1130
5	10	472	460
6	10	528	523
7	10	687	761
8	10	316	256
0	11	1885	1931
1	11	1043	1063
2	11	1057	1014
3	11	382	368
4	11	310	362
5	11	588	611
6	11	622	622
7	11	215	291
0	12	866	914
1	12	1446	1465
2	12	837	881
3	12	713	674
4	12	669	702
5	12	502	518
6	12	504	549
7	12	566	577
0	13	615	558
1	13	547	594
2	13	490	511
3	13	621	675
4	13	315	317
5	13	856	924
6	13	450	479
0	14	88	41
1	14	234	232
2	14	358	383
3	14	392	438
4	14	625	719
5	14	165	311
0	15	750	795
1	15	254	300
2	15	273	300
3	15	322	378
****L = 4******			
0	0	418	378
1	0	4136	4011
2	0	469	589
3	0	3841	3816
4	0	28	110
5	0	1662	1537
6	0	839	824
7	0	1863	1894
8	0	543	514
9	0	1573	1594
10	0	45	148
0	1	2031	2006
1	1	1797	1507
2	1	4087	4198
3	1	2669	2435
4	1	1010	889
5	1	568	562
6	1	1061	994
7	1	320	407
8	1	1433	1424
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7	5	264	290
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9	5	410	389
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6	8	866	840
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6	2	747	766
7	2	531	507
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6	3	627	692
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7	4	1068	1061
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2	7	710	694
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4	7	1385	1382
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7	7	318	349
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6	8	805	793
7	8	573	611
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2	9	797	839
3	9	787	870
4	9	472	471
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7	9	329	348
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4	10	505	530
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4	1	1226	1215
5	1	1228	1218
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8	4	251	254
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0	1	364	425
1	1	309	260
2	1	824	933
3	1	638	653
4	1	205	237
5	1	221	260
0	2	138	35
1	2	232	287
2	2	670	691
3	2	437	470
4	2	700	738
5	2	241	271
0	3	341	314
1	3	62	93
2	3	405	407
3	3	957	979
4	3	227	224
5	3	370	445
0	4	109	150
1	4	665	730
2	4	326	298
3	4	508	529
4	4	220	301
0	5	533	558
1	5	568	595
2	5	749	786
3	5	302	208
4	5	134	45
0	6	225	128
1	6	370	324
2	6	532	541
3	6	379	409
0	7	47	140
1	7	133	164
2	7	178	293
****L = 13******			
1	0	112	102
2	0	547	596
3	0	133	114
0	1	396	449
1	1	65	168
2	1	447	468
3	1	737	756
0	2	146	167
1	2	744	801
2	2	132	225
3	2	343	311
0	3	494	550
1	3	66	138
2	3	627	718
3	3	244	326
0	4	115	171
1	4	211	244
2	4	463	459
0	5	608	639
1	5	68	29

Two more cycles of refinement of all major atom coordinates and anisotropic temperature factors brought the residual to 0.091. Another two cycles of full-matrix refinement in which the scale factor was also a variable caused the residual to drop to 0.065 with no significant changes in any of the varied parameters from the penultimate to the ultimate cycle. The observed and calculated structure factors, $|F_o|$ and F_o, are given in Table I. The final atomic positional coordinates are given in Table II

TABLE II

FINAL ATOM POSITIONAL PARAMETERS[a] FOR dienCr(CO)$_3$

Atom	Coordinates		
	x/a	y/b	z/c
Cr	0.3095(2)	0.3900	0.8065
C_1	0.469	0.424	0.688
C_2	0.465	0.404	0.933
C_3	0.293	0.542	0.812
O_1	0.570	0.457	0.616
O_2	0.572	0.417	1.006
O_3	0.301	0.642	0.804
N_1	0.108	0.358	0.940
N_2	0.115	0.359	0.665
N_3	0.327	0.207	0.778
C_4	−0.048	0.340	0.875
C_5	−0.038	0.393	0.731
C_6	0.112(2)	0.240	0.614
C_7	0.264(2)	0.181	0.644

[a] Standard deviations are all one unit in the last recorded figure except as indicated by a number >1 in parentheses.

and the components of the anisotropic thermal vibration tensors in Table III. The bond lengths and bond angles are recorded in Tables IV and V, respectively. Figure 1 shows a perspective view of the molecule with identifying numbers on the atoms.

TABLE III

ANISOTROPIC THERMAL PARAMETERS[a] (×10^3) FOR dienCr(CO)$_3$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	6.6	2.9	4.7	0.2	0.0	0.1
C_1	9	4	7	0.3	−0.1	−0.6
C_2	10	3	6	0.2	−0.5	0.1
C_3	8	4	11	1	−0.4	−0.6
O_1	15	6	11	−1	4	0.6
O_2	15	7	9	−0.5	−5	−1
O_3	16	4	26	0.4	−2	−0.9
N_1	10	5	7	−0.5	0.7	−0.1
N_2	9	6	6	0.3	−3	−0.3
N_3	13	3	8	0.6	−0.4	0.2
C_4	9	11	9	−0.1	0.2	2
C_5	7	9	14	2	−0.5	2
C_6	22	6	17	4	−10	−5
C_7	15	6	10	1	−2	−4

[a] Standard deviations for Cr, 1 × 10^{-4}; for all other atoms, 1-2 × 10^{-3}.

TABLE IV

BOND LENGTHS (A) IN dienCr(CO)$_3$

Bond	Length[a]	Bond	Length[a]
Cr–C_1	1.822 ± 0.008	C_1–O_1	1.173 ± 0.011
Cr–C_2	1.822 ± 0.008	C_2–O_2	1.162 ± 0.011
Cr–C_3	1.804 ± 0.007	C_3–O_3	1.183 ± 0.009
Cr–N_1	2.185 ± 0.007	N_1–C_4	1.467 ± 0.012
Cr–N_2	2.187 ± 0.007	N_2–C_5	1.495 ± 0.012
Cr–N_3	2.183 ± 0.006	N_2–C_6	1.488 ± 0.013
C_4–C_5	1.579 ± 0.016	N_3–C_7	1.474 ± 0.012
C_6–C_7	1.478 ± 0.016		
Mean values			
Cr–N(av)	2.185 ± 0.004		
Cr–C(av)	1.816 ± 0.005		

[a] Uncertainty intervals are standard deviations of individual values or of the mean, as appropriate.

Discussion

The symmetry of the CrN$_3$(CO)$_3$ portion of Cr(dien)(CO)$_3$ is approximately C_{3v}. The three Cr–N and the three Cr–CO distances are equal within the experimental uncertainties, as would be expected. The crystal and molecular structures of this compound are practically identical with those of Mo(dien)(CO)$_3$, which were recently reported.[5] It is to be noted, however, that the structure of the chromium compound was solved independently without any reference to that of the molybdenum compound.

TABLE V

BOND ANGLES[a] (DEG) IN dienCr(CO)$_3$

C_1CrC_2	85.3 ± 0.4	N_3CrC_1	94.7 ± 0.3
C_2CrC_3	86.5 ± 0.4	N_3CrC_2	97.9 ± 0.3
C_1CrC_3	81.7 ± 0.4	N_1CrC_1	176.1 ± 0.3
N_1CrN_2	78.7 ± 0.3	N_2CrC_2	174.6 ± 0.3
N_2CrN_3	78.2 ± 0.3	N_3CrC_3	174.2 ± 0.4
N_1CrN_3	87.6 ± 0.3	CrC_1O_1	173.3 ± 0.8
N_1CrC_2	97.6 ± 0.3	CrC_2O_2	174.3 ± 0.7
N_1CrC_3	95.8 ± 0.4	CrC_3O_3	170.8 ± 0.9
N_2CrC_1	98.5 ± 0.3	CrNC (av)	112 ± 5
N_2CrC_3	97.8 ± 0.3	NCC (av)	111 ± 3

[a] Uncertainty intervals are standard deviations.

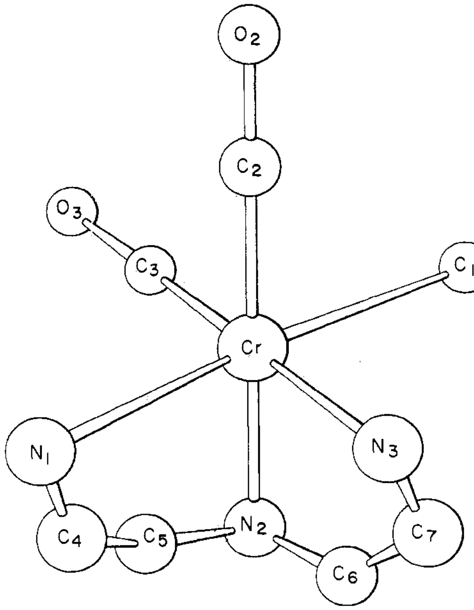

Figure 1.—A perspective view of the dienCr(CO)$_3$ molecule, with atoms numbered as in Tables II–V. There are no crystallographic symmetry elements present.

The mean Cr–CO distance in Cr(dien)(CO)$_3$, 1.817 ± 0.006 A, is markedly shorter than that in Cr(CO)$_6$ (1.91 ± 0.02 A), and a substantial increase in the extent of metal–carbon π bonding is unmistakeably demonstrated, as expected.[15]

Finally, it is to be noted that the mean of the Cr–N distances in the compound is 2.185 ± 0.004 A. This mean value will be used in all subsequent discussions.

The Single-Bond Radius of Chromium(0).—One of the fundamental but difficult problems in connection with formulating detailed descriptions of the bonding in metal carbonyls and other compounds of formally zerovalent metals is the estimation of appropriate single-bond radii of the metals. One of the major objectives of the investigation reported here was to do this for

(15) A semiquantitative interpretation similar to that given earlier[5] for the molybdenum compounds could also be made here. However, in view of the suggestions made by Dobson[9] for modification of the numerical values to be assumed for the π-bond orders, with which we at least partially agree, further quantitative discussion will be deferred.

Cr(0). Formally zerovalent metal atoms can be expected to occur only when surrounded by a considerable number of ligands capable of accepting electrons from dπ orbitals of the metal (that is, ligands which are π acids), and, of course, the lengths of such bonds, which have multiple bond character, cannot be used to derive a single-bond radius for the metal.

However, it is reasonable to assume that when one or several π acid ligands, such as CO, are replaced by ligands which are simple donors but not π acids, such as NH_3 and amines, *and* sufficient π acid ligands remain to stabilize the molecule, the bonds to the amine ligands will be simple single bonds and their lengths will be the sum of the nitrogen tetrahedral radius,[16a] 0.70 A, and the metal atom single-bond radius. Thus, from the average of the Cr–N distances in $Cr(dien)(CO)_3$, 2.18 ± 0.01 A, we estimate a Cr(0) single-bond radius of 1.48 ± 0.02 A. This may be compared with a single-bond radius of about 1.62 A, which can be estimated in the same way for Mo(0) in $Mo(dien)(CO)_3$ from the structural data recently published for that compound.[5]

It has been shown[4] from the CO stretching force constants that the extent of back donation in analogous carbonyl derivatives of Cr, Mo, and W is approximately the same. Thus the difference in radii, 0.14 A, should be approximately reflected in the differences between Cr–CO and Mo–CO distances in analogous pairs of compounds. This is the case in both the $M(dien)(CO)_3$ compounds, where the difference is $1.94 - 1.82 = 0.12$ A, and the hexacarbonyls, where it is $2.04 - 1.92 = 0.12$ A.

Finally, it may be noted that the Cr–CO and Mo–CO bonds are about 0.27 and 0.35 A shorter than would be expected for M–C single bonds in the $M(CO)_6$ and $M(dien)(CO)_3$ compounds, respectively. These shortenings are considerably greater than the ~0.1 A proposed by Pauling[16b] on the basis of unspecified assumptions as to the single-bond radii and suggest that his statement that "the bonds have some double-bond character" might well be made more emphatic.

The Radius of Mn in Derivatives of $Mn(CO)_5$.—The Cr radius in $dienCr(CO)_3$ can be obtained by subtracting the nitrogen radius, 0.70 A, from the mean Cr–N distance, 2.18 ± 0.01 A, giving 1.48 A, as noted above. Since we should naturally assume that the manganese atom is inherently smaller than the chromium atom due to its greater nuclear charge, we must regard this as an upper limit on the Mn(0) radius. More specifically, comparing the mean Mn–CO distance[17] in $HMn(CO)_5$ with that[18] in $Cr(CO)_5NH_3$, in which all factors save the inherent size of the metal atom should be essentially the same, it is found that the Mn radius is, in fact, about 0.05 A smaller than that of Cr. Thus, we may establish an upper limit of ~1.43 A for the Mn radius. This is in substantial agreement with one-half the Mn–Mn distance in $Mn_2(CO)_{10}$, 1.46 A, which is also to be considered an upper limit because of some repulsive force between the dπ electrons of the two metal atoms.[6,19]

It is even possible, using the CO stretching force constants for $HMn(CO)_5$[20] and for $Cr(CO)_5NH_3$[21] and the relations between M–C bond lengths, M–C and C–O bond orders, and CO stretching force constants which have been previously described,[3–5] to estimate that Mn–C bond lengthening relative to the Cr–C bonds, because of lower back donation, is probably about 0.05 A. Thus, the Mn radius would seem likely to be about 1.39 A.

Relevance to Metal–Arene Bonding.—The present results, specifically the metal-to-carbon bond lengths in $dienCr(CO)_3$, afford some information concerning the electron distribution in chromium-to-benzene bonding, at least as it occurs in the $(C_6H_6)Cr(CO)_3$ and $[(CH_3C)_6]Cr(CO)_3$ molecules. Each of these has recently been studied by Bailey and Dahl.[22] Aside from the general similarity of the dimensions of the $Cr(CO)_3$ groups in these two compounds to each other and to those of the $Cr(CO)_3$ group in $Cr(dien)(CO)_3$, the essential equality of the mean Cr–C distances in the three compounds is especially noteworthy. For the benzene, hexamethylbenzene, and dien compounds, the mean Cr–C distances and the standard deviations of the mean are, respectively, 1.842 ± 0.007, 1.814 ± 0.007, and 1.816 ± 0.005 A. If it be accepted that the dien group entirely lacks the capacity to back-accept dπ electrons from the metal atom, then these results imply that the benzene and hexamethylbenzene rings fail to do so even though they may in principle be capable of doing so by means of their e_2 orbitals. Of course, this conclusion is only valid provided one also assumes that the Cr–CO σ bonding is very similar in character in both the arene and dien complexes, but such an assumption seems plausible and there are no data available which contradict it.

Acknowledgment.—We thank the MIT Computation Center for the use of the IBM 7094 computer.

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[16] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960: (a) Table 7-13, p 246; (b) p 335.

[17] S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2282 (1964).

[18] F. C. Rauch, Thesis, Massachusetts Institute of Technology, 1964.

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[20] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

[21] The spectrum shows four bands (in $CHCl_3$) at 2065, 1980, 1935, and 1885 cm^{-1}. From these, the force constants[3,4] are found to be $k = 14.6$, $k_2 = 15.8$, $k_i = 0.33$ mdyne/A.

[22] M. F. Bailey and L. F. Dahl, *Inorg. Chem.* **4**, 1298, 1314 (1965).