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Carbon and Oxygen Coordinated Carbon Monoxide. Preparation and Structure of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2.2Al(C_2H_5)_3$

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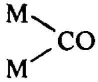
The interaction of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ *with* $[Al(C_2H_5)_3]_2$ *in hydrocarbon solution produces a 1:1 adduct which may be isolated as air-sensitive red chystals. Adduct formation is accompanied by a 112* cm^{-1} *reduction in the asymmetric stretching frequency of the bridging carbonyls. Infrared, molecular weight and nmr data indicate that the adduct is partially dissociated in hydrocarbon solution. By means of x-ray single crystal diffraction the compound was found to crystallize in space group C2/c with four molecules in a unit cell of dimensions a = 14.45(2), b = 14.12(2), c = 14.70(3) Å, and β = 100° 50(15)′. The structure was refined to a convential R factor of 12% over 815 reflections collected on film. The structure involves a* cis$[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ *moiety cordinated to two trithylaluminum acceptors through the oxygen of each bridging carbonyl. The Al-O bond distance is 1.98 Å.*

Introduction

Since the x-ray diffraction structure determination of $Fe_2(CO)_9$ by Powell and Ewens in 1939[2] it has been recognized that metal carbonyls may contain metal-carbon bridging CO groups,  $\overset{M}{\underset{M}{>}}CO$. The possibility of bridging through both carbon and oxygen has been discussed by various authors,[3-5] but the first definitive report of this phenomenon appeared only recently in a preliminary communication of the present work.[6] This research on the basicity of the bridging carbonyl group was prompted by analogy[4] with ketones which are well known Lewis bases.

Experimental Section

Preparations. Schlenk, syringe, dry-box and vacuum-line techniques[7] were used to exclude air in the preparation and handling of $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2 \cdot 2Al(C_2H_5)_3$. In a typical preparation, 2.5 g (7.06 mmole) of pure $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$[8] was degassed in a Schlenk tube, and 100 ml of thoroughly dry and oxygen-free toluene was added under nitrogen. To this suspension 2.1 ml of $Al(C_2H_5)_3$,(15 mmole) was added followed by stirring overnight. Removal of solvent under vacuum left a thick liquid to which 300 ml of dried and degassed heptane was added. After stirring for 30 minutes, the fine bright red crystals which formed were collected under nitrogen, washed with three 50 ml portions of dried and degassed hexane, and dried by brief exposure to vacuum. *Anal.* Calcd. for $C_{26}H_{40}Al_2Fe_2O_4$: C_2H_6, 28.22; Fe, 19.2 Found: C_2H_6, 28.64; Fe, 20.5. Ethane was determined by hydrolysis[9] and iron was determined poteniometrically with cerium(IV) sulfate.[10] The molecular weight in benzene solution varied with concentration: 428 for 1.72 mg sample/g benzene, 475 for 4.17 mg sample/g benzene and 505 for 5.67 mg sample/g benzene; (Calcd. 582). The density of the crystal determined on the vacuum line by He displacement is 1.31 g cm^{-3}. In the presence of excess triethylaluminum infrared absorptions are found at 2042s, 2004s and 1682s cm^{-1} for freshly prepared heptane solutions at –3°. In the absence of excess triethylaluminum, a more complex spectrum is observed, indicating significant dissociation. The nmr spectrum which also is somewhat concentration dependent is τ 5.62 (singlet) 8.43 (triplet) and 9.51 (quartet) with relative intensities 9.6:18:13.1; in reasonable agreement with the expected ratios of 10:18:12 for C_2H_5, CH_3 and CH_2 respectively.

Crystallography. A crystal of the adduct in a quartz capillary was examined by Weissenberg and procession x-ray photographs, and found to have monoclinic symmetry with a = 14.45(2), b = 14.12(2), c = 14.70(3) Å, and β = 100° 50(15)′. Systematic absences of hkl, h + k ≠ 2n and h0l, l ≠ 2n, is consistent with space group C2/c or Cc. The presence of a large number of Harker peaks for the 2x, 0, 1/2 + 2z plane in the three-dimensional Patterson function indicate the centrosymmetric space group C2/c. From the

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(1) Formerly N.E. Kime.
(2) H.M. Powell and R.V.G. Ewens, *J. Chem. Soc.*, 286 (1939).
(3) N.V. Sidgwick and R.W. Bailey, *Proc. Roy. Soc.*, *A 144*, 521 (1934); R.V.G. Ewens and M.W. Lister, *Trans. Faraday Soc.*, *35*, 681 (1939).
(4) C.C. Barraclough, J. Lewis, and R.S. Nyholm, *J. Chem. Soc.*, 2582 (1961); G. Dobson and R.K. Scheline, *Inorg. Chem.*, *2*, 1313 (1963).
(5) G.W. Parshall, *J. Amer. Chem. Soc.*, *86*, 361 (1964); K.F. Purcell, *ibid.*, *91*, 3487 (1969).
(6) N.J. Nelson, N.E. Kime, and D.F. Shriver, *J. Amer. Chem. Soc.*, *91*, 5173 (1969).
(7) D.F. Shriver, « The Manipulation of Air-Sensitive Compounds », McGraw Hill Book Company, New York, N.Y., 1969.
(8) T.S. Piper, F.A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *1*, 165 (1955).
(9) Ref. 7, page 81.
(10) D.A. Skoog and D.M. West, « Fundamentals of Analytical Chemistry », Holt, Rinhart, and Winston, New York, N.Y., 1963, page 451.

Table I. Final Atomic and Thermal Parameters.

Atom^a	X	Y	Z	$10^4\beta_{11}$ or B	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10_1\beta_{23}$
Fe	0.0167(2)	0.1699(2)	—0.1637(2)	50(2)	49(2)	45(2)	2(3)	5(1)	0(2)
Al	0.2913(6)	0.1213(6)	—0.3069(7)	73(7)	114(8)	98(8)	30(6)	28(6)	6(6)
C_1	0.0916(19)	0.1999(19)	—0.0343(19)	7.2(8)					
C_2	—0.0069(19)	0.2106(19)	—0.0343(18)	6.3(7)					
C_3	—0.0373(19)	0.2842(18)	—0.0985(19)	6.1(7)					
C_4	0.0455(18)	0.3134(19)	—0.1315(17)	5.9(7)					
C_5	0.1201(20)	0.2585(20)	—0.0899(21)	7.5(8)					
C_b	0.0976(16)	0.1534(15)	—0.2492(15)	4.3(5)					
O_b	0.1798(11)	0.1413(10)	—0.2493(10)	5.6(4)					
C_t	0.0202(17)	0.0526(17)	—0.1370(15)	4.4(6)					
O_t	0.0203(12)	—0.0304(13)	—0.1235(11)	7.1(5)					
C_{11}	0.3680(20)	0.0368(19)	—0.2184(21)	7.6(8)					
C_{12}	0.4231(27)	0.0799(25)	—0.1314(27)	11.9(12)					
C_{21}	0.3233(25)	0.2476(24)	—0.3323(27)	11.3(11)					
C_{22}	0.3299(22)	0.3138(26)	—0.2582(24)	10.5(10)					
C_{31}	0.2223(28)	0.0407(27)	—0.4170(29)	12.4(12)					
C_{32}	0.2661(36)	0.0183(35)	—0.4793(36)	16.5(16)					

^{a} X, Y and Z are the fractional coordinates. The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l_2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Standard deviations of the least significant figures are reported in parentheses. C_{11}, C_{21} and C_{31} are the three methylene carbons attached to Al. C_{12}, C_{22} and C_{32} are the methyl carbons associated with the respective methylene carbons, and C_1 through C_5 are carbons of the cyclopentadienyl group. The molecule possesses 2 symmetry.

Table II. Bond Lenghts and Angles^a.

Atoms^a	Length Å	Atoms^a	Angle, deg
Fe-Fe	2.491(8)	Fe-C_t-O_t	176(2)
Fe-C_1	2.05(3)	Fe-C_b-O_b	139(2)
		Fe-Fe'-C_t	102.5(8)
Fe-C_2	2.08(3)	C_b-O_b-Al	155(2)
Fe-C_3	2.10(3)	O_b-Al-C_{11}	102(1)
Fe-C_4	2.10(3)	O_b-Al-C_{21}	101(1)
Fe-C_5	2.09(3)	O_b-Al-C_{31}	96(1)
Fe-C_b	1.88(2)		
Fe-C_t	1.70(2)	Fe-C_b-Fe': Fe-C_b'-Fe'^{b}	167(1)
C_b-O_b	1.20(2)		
C_t-O_t	1.19(2)		
Al-O_b	1.98(2)		
C_1-C_2	1.43(3)		
C_2-C_3	1.42(3)		
C_3-C_4	1.43(3)		
C_5-C_1	1.28(3)		
Al-C_{11}	1.95(3)		
C_{11}-C_{12}	1.50(4)		
Al-C_{21}	1.90(3)		
C_{21}-C_{22}	1.42(4)		
Al-C_{31}	2.07(4)		
C_{31}-C_{32}	1.25(5)		

^{a} See Figure 1 and footnotes to Table I for numbering scheme. ^{b} Dihedral angle between the Fe-C_b-Fe' and Fe-C_b'-Fe' planes.

observed denisty of 1.31 g cm^{-3}, Z equals 4 (ρ_{calc} = 1.31 g cm^{-3}).

Data Collection and Reduction. A crystal of approximately cubic habit, 0.1 × 0.1 × 0.08 mm^3, was mounted along its [$\bar{1}10$] axis in a quartz capillary. Six layers of equi-inclination Weissenberg photographs were taken at room temperature using Zr filtered MoK$_\alpha$ radiation. Intensities of the reflections were estimated visually and were corrected for Lorentz and polarization effects but not absorption since the linear absorption coefficient for MoK$_\alpha$ is 11 cm^{-1}. The data were interscaled by comparison of common reflections to yield structure amplitudes for 815 reflections.

Iron and aluminum positions were found in the Patterson map and were used as trial coordinates for two cycles of least-squares refinement. A difference Fourier map then gave the positions of all remaining nonhydrogen atoms. These were included in further least-squares refinement using isotopic temperature factors.

Throughout the analysis, the atomic scattering factors used for Al, C and O were those tabulated by Ibers,[11] and the scattering factors for Fe were those of Cromer and Waber.[12] Cromer's values were used for the anomalous dispersion terms[13] $\Delta f'$ and $\Delta f''$. The function minimized in the least squares refinement was $\Sigma w(|F_o|-|F_c|)^2$. Anisotropic thermal parameters for Fe and Al were employed and hydrogen atoms were introduced as fixed contributions, with methyl hydrogens included in a ring to approximate a free rotor. Scattering factors for hydrogen were those of Stewart, *et al.*[14] The final agreement factors for all reflections having $F > 2\sigma$ are $R_1 = \Sigma(||F_o|-F_c||)/\Sigma|F_o| = 0.12$, and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2)^{1/2} = 0.12$, where $|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes respectively, and $w = 256/F_o^2$ for $I > 16$ and $w = I^2/F_o^2$ for $I \leqslant 16$ with I being the raw intensity. Final atomic and thermal parameters are given in Table I, bond lengths and bond angles are given in Table II, and observed and calculated structure factors appear in Table III.

For most of the carbon atoms in the ethyl groups rather high thermal parameters are found. One methyl carbon in particular, C_{32}, has a very high temperature factor and at least one additional peak due to this carbon can be found in the difference Fourier. As with many compounds containing ethyl groups, disorder is indicated. From a consideration of the number of data points and parametrs, it was inadvisable to explore the nature of this disorder. Bond lengths associated with ethyl group 3 are to be disregarded.

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(11) J.A. Ibers in « International Tables of X-ray Crystallography », vol. 3, The Kynoch Press, Birmingham, England, Table 3.3.1 A.

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

(13) D.T. Cromer, *ibid.*, *17*, 781 (1964).

(14) R.F. Stewart, E.R. Davidson, and W.T. Simpson, *J. Chem. Phys.*, *42*, 3175 (1965).

Table III. Observed and Calculated Structure Factors for $[(h^5C_5H_5)Fe(CO)_2]_2 . 2Al(C_2H_5)_3$.

H	L	FO	FC
***** K = 0 *****			
-10	2	1390	1298
-10	4	828	727
-10	6	570	636
-10	8	788	698
-8	2	420	530
-8	6	1209	1291
-8	8	841	796
-8	12	508	501
-6	2	2344	2275
-6	4	1177	1144
-6	6	781	685
-6	8	555	687
-6	10	393	295
-4	4	2036	1976
-4	6	2642	2163
-4	8	961	914
-4	12	567	496
-2	2	733	806
-2	4	2068	2074
-2	6	1357	1295
-2	10	549	592
0	4	998	966
0	6	927	924
0	10	664	636
0	12	497	527
2	0	1021	2004
2	2	1150	1161
2	4	2673	2661
2	6	1417	1362
2	8	735	575
2	10	918	775
4	0	2234	2098
4	2	357	364
4	4	1373	1404
4	6	991	1016
4	10	336	336
6	0	1553	1591
6	2	175	291
6	4	2023	1899
6	6	719	759
6	8	307	376
6	10	393	472
8	0	657	386
8	2	763	804
8	4	865	895
10	0	953	797
10	2	290	436
10	4	958	354
10	8	397	254
10	10	464	340
***** K = 1 *****			
-11	1	577	487
-11	2	569	537
-11	3	570	574
-11	4	278	158
-11	5	283	114
-11	6	290	319
-11	7	471	538
-9	1	579	571
-9	2	681	518
-9	3	667	783
-9	5	237	233
-9	6	301	200
-9	7	445	554
-9	9	352	256
-7	1	825	843
-7	2	846	865
-7	3	373	650
-7	4	267	330
-7	5	483	521
-7	6	1064	1044
-7	7	1243	1476
-7	8	398	345
-7	9	546	578
-7	13	452	378
-5	1	584	846
-5	2	742	753
-5	3	564	547
-5	4	650	634
-5	5	403	519
-5	6	610	675
-5	7	1104	1010
-5	10	399	395
-5	11	572	592
-5	13	378	362
-3	1	3709	3360
-3	2	2005	1877
-3	3	776	704
-3	4	590	548
-3	5	984	1066
-3	6	1093	1124
-3	7	1470	1386
-1	3	1694	1585
-1	5	1120	1098
-1	6	805	807
-1	7	930	882
-1	9	390	404
-1	10	612	614
-1	11	696	680
-1	12	384	414
-1	13	474	499
1	2	564	557
1	3	552	443
1	4	636	620
1	7	354	410
1	8	234	227
1	9	422	423
1	11	477	467
1	13	357	312
3	0	1917	1578
3	1	1021	980
3	2	1188	984
3	3	1125	1035
3	4	1145	1153
3	5	1787	1630
3	6	1109	1126
3	7	821	966
3	9	398	265
5	0	1100	1066
5	1	274	288
5	2	309	214
5	3	894	1039
5	4	872	814
5	5	1075	1051
5	6	280	183
5	8	467	444
5	9	539	613
5	10	380	348
5	11	334	338
7	0	845	935
7	1	741	787
7	2	297	174
7	3	663	753
7	4	632	610
7	5	888	772
7	6	239	269
9	0	240	214
9	2	609	637
9	3	930	891
9	4	769	686
9	5	549	489
9	8	436	391
9	10	306	182
11	0	438	496
11	9	406	324
***** K = 2 *****			
-12	1	435	306
-12	2	475	214
-12	3	499	330
-12	4	321	377
-12	8	347	245
-10	1	997	1022
-10	3	902	896
-10	7	513	528
-10	8	262	229
-10	9	373	336
-8	1	366	414
-8	4	384	474
-8	5	643	704
-8	7	901	793
-8	8	441	486
-8	9	277	236
-6	1	1224	1045
-6	3	1152	1141
-6	4	485	504
-6	6	478	513
-6	7	483	455
-6	8	551	689
-6	12	366	369
-4	1	865	990
-4	2	343	384
-4	3	377	376
-4	4	257	168
-4	5	1193	1344
-4	6	645	541
-4	7	1307	1311
-4	8	702	726
-4	9	474	432
-4	11	357	408
-4	13	469	436
-2	0	1609	1466
-2	1	692	629
-2	2	316	275
-2	3	177	192
-2	4	604	404
-2	5	489	455
-2	6	444	369
-2	7	733	757
-2	8	470	504
-2	11	408	484
-2	12	362	372
-2	13	302	259
0	0	1165	1443
0	1	2932	3011
0	2	480	537
0	3	627	608
0	5	605	460
0	6	686	521
0	7	1060	1034
0	11	609	582
0	12	447	440
0	13	410	375
2	1	294	411
2	2	1820	1796
2	5	1459	1418
2	6	670	719
2	7	654	680
2	8	344	385
2	9	597	606
2	11	720	682
4	1	975	939
4	2	799	670
4	4	205	141
4	5	954	870
4	6	589	640
4	7	666	681
4	11	288	356
4	12	291	166
6	0	676	548
6	2	396	349
6	3	843	855
6	4	439	417
6	5	1032	1093
6	9	282	388
6	10	295	348
6	11	484	448
8	3	541	588
8	4	641	567
10	0	299	231
10	3	436	502
10	5	477	372
10	6	296	170
10	9	377	324
10	11	332	184
12	0	291	102
12	1	264	185
12	3	414	482
12	4	203	99
12	6	301	125
12	9	407	286
***** K = 3 *****			
-13	2	446	403
-13	4	401	319
-11	2	681	496
-11	4	394	262
-11	8	299	333
-11	12	339	250
-9	2	563	487
-9	4	347	399
-9	6	265	347
-9	7	272	330
-9	8	488	419
-7	1	498	473
-7	2	997	849
-7	6	673	743
-7	8	948	767
-7	14	334	345
-5	2	701	719
-5	3	422	361
-5	6	647	580
-5	8	517	506
-5	12	521	548
-3	3	688	769
-3	4	195	345
-3	6	1342	1342
-3	8	1423	1373
-3	9	280	222
-3	12	374	405
-1	0	1893	1883
-1	1	1314	1088
-1	2	1071	984
-1	3	1313	1374
-1	4	349	329
-1	5	300	240
-1	6	1098	1059
-1	8	680	591
-1	10	572	673
-1	11	361	306
-1	12	774	740
-1	14	324	310
1	0	2094	1880
1	1	232	140
1	2	1168	1059
1	3	956	828
1	4	1566	1511
1	6	888	806
1	10	667	690
1	12	648	402
3	1	633	594
3	2	302	224
3	4	1149	1287
3	6	1600	1703
3	8	442	586
3	10	468	479
3	12	463	459
5	0	490	411
5	4	643	600
5	5	429	394
5	6	840	884
5	10	664	667
5	12	400	386
7	0	947	1060
7	2	419	271
7	4	733	743
7	6	635	620
7	10	436	449
9	1	299	334
9	2	360	428
9	4	603	760
9	6	332	378
9	10	315	457
11	0	489	530
11	4	296	298
11	10	410	375
13	0	281	166
13	2	290	341
13	3	348	110
13	4	480	414
***** K = 4 *****			
-12	1	381	453
-12	3	430	363
-10	1	598	470
-10	2	673	666
-10	3	519	450
-10	4	413	401
-10	8	366	277
-8	1	619	607
-8	3	515	452
-8	4	408	376
-8	6	491	455
-8	7	594	477
-6	1	975	977
-6	2	773	773
-6	3	261	221
-6	4	395	471
-6	5	829	875
-6	7	706	688
-6	9	279	342
-4	0	417	296
-4	1	1434	1316
-4	2	405	464
-4	3	451	521
-4	4	520	472
-4	5	521	676
-4	6	805	800
-4	7	911	869
-4	8	888	776
-4	12	364	261
-2	0	194	149
-2	1	1673	1707
-2	2	298	378
-2	3	182	222
-2	5	251	346
-2	6	226	243
-2	7	1086	979
-2	11	472	452
-2	13	400	391
0	1	385	391
0	2	2124	1801
0	3	265	322
0	4	559	429
0	5	403	526
0	6	491	518
0	7	1034	1043
0	11	561	534
0	13	412	406
2	1	610	666
2	4	748	782
2	5	658	695
2	6	859	819
2	7	920	924
2	10	310	304
2	11	355	468
2	12	350	281
4	1	403	513
4	2	616	738
4	3	274	374
4	5	1006	881
4	6	367	334
4	11	409	439
6	1	405	460
6	2	376	428
6	3	555	640
6	5	619	605
6	6	308	342
6	11	399	416
8	3	755	758
8	5	658	598
8	6	341	181
10	0	480	391
10	3	597	467
12	3	398	413
***** K = 5 *****			
-11	1	404	423
-11	2	345	308
-9	1	417	491
-9	2	589	471
-9	3	576	573
-9	6	379	523
-9	7	284	364
-9	8	412	291
-7	1	1202	1061
-7	2	696	362
-7	3	557	685
-7	5	349	493
-7	6	284	328
-7	7	561	714
-7	9	396	419
-5	0	978	911
-5	1	796	907
-5	2	966	955
-5	5	654	678
-5	6	496	570
-5	7	283	340
-5	8	401	445
-5	11	359	323
-5	13	318	342
-3	0	608	635
-3	1	750	566
-3	4	536	521
-3	5	672	715
-3	6	504	566
-3	7	842	879
-3	9	376	397
-1	0	1333	1283
-1	1	1607	1731
-1	2	338	383
-1	3	265	190
-1	4	293	287
-1	5	1106	1063
-1	6	411	460
-1	7	673	676
-1	11	452	525
-1	13	394	335
1	0	1565	1283
1	1	1482	1319
1	3	616	517
1	4	514	583
1	5	671	607
1	6	1160	1162
1	9	437	427
1	10	366	367
1	11	375	486
1	12	338	269
3	0	653	635
3	1	642	684
3	3	889	835
3	5	1235	1207
3	6	558	583
3	7	321	480
5	3	591	670
5	4	599	695
5	5	458	527
5	6	674	681
7	1	300	239
7	2	673	596
7	3	363	450
7	4	662	476
7	5	386	459
9	0	447	585
9	3	372	443
9	4	363	343
11	2	357	403
***** K = 6 *****			
-12	2	388	457
-10	2	621	566
-10	8	309	432
-8	1	572	496
-8	2	590	761
-8	3	562	524
-8	6	589	594
-8	8	463	480
-6	0	654	832
-6	1	236	206
-6	2	1145	1167
-6	3	279	214
-6	4	256	149
-6	5	380	379
-6	6	624	734
-6	7	377	261
-6	8	419	471
-6	12	432	343
-4	0	1141	1000
-4	2	984	879
-4	4	443	458
-4	5	390	409
-4	6	1061	1026
-4	8	563	607
-2	0	1295	1282
-2	1	385	454
-2	2	840	808
-2	4	719	641
-2	6	1191	1167
-2	7	762	660
-2	8	414	537
-2	9	263	79
-2	10	411	372
-2	12	302	451
0	0	2069	1896
0	1	825	895
0	2	1050	1018
0	3	491	422
0	6	777	720
0	7	521	497
0	10	424	572
0	12	402	466
2	1	540	555
2	2	336	395
2	3	887	830
2	4	987	918
2	6	898	985
2	7	490	298
4	0	1121	1060
4	1	421	345
4	2	669	546
4	4	1055	1160
4	6	694	647
6	4	601	716
6	6	454	364
8	2	427	381
8	4	671	673
10	0	419	326
10	4	367	353
***** K = 7 *****			
-11	3	484	472
-9	1	583	560
-9	2	358	306
-9	3	546	576
-9	7	389	563
-7	0	402	227
-7	1	477	426
-7	3	265	496
-7	6	375	221
-7	7	533	587
-7	8	320	437
-5	1	1105	1120
-5	3	334	318
-5	5	515	602
-5	7	741	872
-5	9	355	426
-3	1	975	966
-3	4	226	263
-3	5	549	529
-3	6	331	366
-3	7	592	615
-3	8	491	331
-3	11	544	528
-1	0	594	599
-1	1	1102	1074
-1	2	314	325
-1	3	413	498
-1	4	430	400
-1	5	572	509
-1	7	626	778
-1	11	361	444
1	0	615	599
1	1	893	902
1	2	569	588
1	3	466	557
1	4	370	231
1	5	1394	1311
1	6	246	132
1	7	685	705
1	9	437	304
1	11	463	451
1	13	356	225
3	0	290	252
3	1	607	567
3	4	653	685
3	5	662	583
3	6	390	440
5	1	562	606
5	3	353	506
5	5	814	784
5	7	483	322
7	3	500	583
7	5	400	480
7	9	308	354
9	3	366	306
9	5	383	301
11	3	429	405
***** K = 8 *****			
-10	2	315	129
-8	0	436	387
-8	1	393	388
-8	2	686	731
-8	3	281	274
-8	6	358	304
-8	8	358	286
-8	9	443	307
-6	0	374	359
-6	1	417	517
-6	2	335	420
-6	4	269	207
-6	6	594	626
-6	7	544	490
-4	0	465	617
-4	1	333	344
-4	2	725	640
-4	5	396	449
-4	7	488	539
-2	0	1310	1264
-2	1	565	601
-2	2	661	628
-2	3	215	193
-2	4	622	431
-2	5	567	690
-2	6	793	740
-2	7	580	551
-2	8	257	336
0	0	707	545
0	1	916	981
0	3	309	299
0	4	572	551
0	5	380	326
0	6	567	527
0	7	307	105
0	10	661	333
0	11	396	449
2	0	1340	1294
2	1	583	532
2	2	460	486
2	4	341	350
2	5	641	661
2	6	526	527
2	11	449	346
4	2	318	332
4	3	656	502
4	4	725	788
4	5	603	729
4	6	327	368
6	4	439	291
6	5	574	614
8	3	278	298
8	4	401	377
8	5	411	478
8	10	334	178
***** K = 9 *****			
-11	2	604	495
-9	2	484	588
-9	8	442	416
-7	2	404	453
-7	4	423	372
-7	6	313	343
-5	0	728	815
-5	1	407	425
-5	2	807	724
-5	5	270	274
-5	7	496	616
-5	8	503	543
-3	0	655	702
-3	1	293	347
-3	2	317	451
-3	4	472	491
-3	6	739	724
-1	0	1057	1111
-1	1	525	384
-1	2	839	770
-1	4	275	270
-1	5	275	165
-1	6	515	450
1	0	1100	1111
1	2	374	367
1	3	383	390
1	4	863	820
1	5	409	335
1	6	661	679
1	10	446	321
1	12	438	364
3	4	666	650
3	6	605	679
5	4	697	761
5	6	472	541
7	3	305	239
7	4	675	635
9	4	571	402
***** K = 10 *****			
-10	2	323	238
-8	1	601	573
-8	2	376	229
-8	3	420	439
-6	1	260	395
-6	5	354	443
-6	6	416	216
-6	7	497	519
-4	1	601	657
-4	3	312	322
-4	4	410	184
-4	5	322	237
-4	6	269	293
-4	7	353	294
-2	0	376	174
-2	1	943	924
-2	5	512	570
-2	6	354	341
-2	7	492	389
0	0	470	464
0	1	389	453
0	2	388	412
0	5	685	678
0	7	401	264
0	11	505	309
0	13	330	182
2	5	515	560
2	7	298	279
2	11	344	267
4	3	349	362
4	4	357	275
4	5	634	693
***** K = 11 *****			
-5	1	419	526
-3	0	366	247
-3	1	410	310
-3	5	427	590
-3	6	335	180
-1	0	429	307
-1	1	542	671
-1	5	257	348
1	1	471	446
1	4	296	166
1	5	601	419
1	6	401	358
1	7	364	165
3	5	300	351
3	6	308	217
5	5	506	419
***** K = 12 *****			
-4	0	353	267
-4	2	275	384
-4	6	291	330
-2	0	379	461
-2	2	356	455
-2	8	297	198
2	6	413	351
2	8	358	150
4	10	467	193
4	4	403	317
***** K = 13 *****			
-3	1	281	374

Results and Discussion

Composition. As outlined in the Experimental Section, Fe and C_2H_5 analyses as well as nmr results indicate a 1:2 adduct, $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2\cdot 2Al(C_2H_5)_3$, this composition is confirmed by results of a tensimetric titration with trimethyl amine which show that two moles of trimethyl amine are consumed per mole of adduct in accord with the following displacement reaction (eq. 1)

$$[(h^5\text{-}C_5H_5)Fe(CO)_2]_2 . 2Al(C_2H_5)_3 + 2N(CH_3)_3 \rightarrow 2Al(C_2H_5)_3 . N(CH_3)_3 + [(h^5\text{-}C_5H_5)Fe(CO)_2]_2 \qquad (1)$$

Furthermore, quantitative regeneration of the parent iron complex is observed when this reaction is monitoret in heptane solution by infrared absorption in the CO stretch region. Similarly the compound $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2\cdot 2Al(CH_3)_3$ was synthesized on the vacuum line (1.98 trimethylaluminum per iron dimer determined by weight gain and 18.4% CH_3 by hydrolysis; calc. 18.1%).[15] During formation of the trimethylaluminum adduct, the reaction tube was constantly monitored for non-condensable gases such as CO, with negative results. Despite the high reactivity of these adducts and the associated difficulty of analysis, their composition is established beyond reasonable doubt. The indication of dissociation from spectral measurements and removal of trithylaluminum from the adduct by trimethylamine demonstrate weak nature of the bridging carbonyl trithylaluminum interaction.

Structure. The most important result of the determination is coordination of trithylaluminum to the oxygens of the bridging carbonyls (Figure 1). The Al-O distance 1.98(2) Å is close to the value 2.02(2) Å observed for the donor-acceptor bond in the bis-trimethylaluminum-dioxane adduct,[16] but is significantly longer than the Al-O distance of 1.89 Å in [Al-

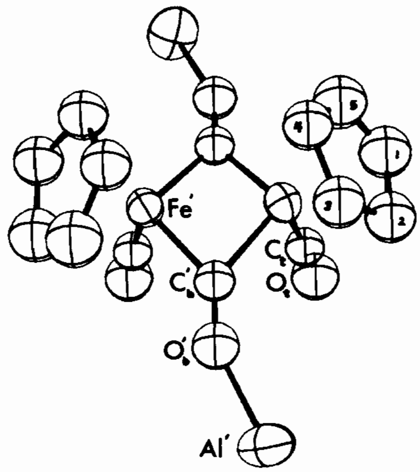

Figure 1. The structure of $[(h^5C_5H_5)Fe(CO)_2]_2 . 2Al(C_2H_5)_3$. Ethyl groups and hydrogen atoms have been omitted from the figure to improve clarity. Fe and Al were refined anisotropically while C and O were refined with isotropic thermal parameters. Primed atoms are related to unprimed atoms by a two-fold axis. The Fe-Fe bond, which is required by simple valence considerations, has been omitted for clarity.

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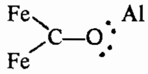
(15) This adduct readily loses trimethylaluminum under vacuum and because of this complication it was not chosen for the structural work.

(16) J.L. Atwood and G.D. Stucky, *J. Amer. Chem. Soc.*, 89, 5362 (1967).

$(H_2O)_6]^{3+}$,[17] and 1.82 Å in $AlCl_3 \cdot C_6H_4COCl$.[18] The Al-O-C bond is bent (155°) in a fashion similar to that found $AlCl_3 \cdot C_6H_4COCl$. The Al-C bond distances with range between 1.89(3) and 2.07(4) Å are comparable to the average value of 1.97 Å the adduct $Al(CH_3)_3C_4H_8O_2$.[16] Thus, the structural features are consistent with relatively weak donor-acceptor interaction between the oxygen end of carbon monoxide and trithylaluminum. Within the calculated standard deviations, the Fe, C_b, O_b and Al atoms lie in a plane.[19] Whether the position of the aluminum atom is primarily determined by bonding or packing forces is unknown, however, it is consistent with that expected for disposition of the lone pairs:



Recently the structure of *cis*$[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ has been determined[20] and that of the *trans* isomer has been redetermined with high accuracy.[21] Little difference was found between the molecular dimensions of the forms. The present results are less accurate than those of the parent isomers because our data set, which is more limited, was collected on film rather than on a diffractometer and because of disorder of the ethyl groups in our compounds. The Fe-Fe bond distance (Table II)is 0.04 Å shorter in the adduct which is significantly greater than the combined standard deviation for the two structures (0.008 Å).[22] Another small, but apparently significant difference is an increase in the dihedral angle between the two Fe_2C_b planes from 164° in the parent to 167(1)° in the adduct. All other differences between the parent and the adduct fall close to or within the standard deviations and therefore cannot be considered significant. As with the inferences from chemical information and the Al-O bond length, the small perturbation of the $[(h\text{-}C_5H_5)Fe(CO)_2]_2$ moiety indicates weak donor-acceptor interaction in the adduct.

Stability. The $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2 \cdot 2AlEt_3$ adduct although susceptible to easy removal of triethylaluminum is stable in the solid state for at least several months. This stability contrast with the behaviour of organic carbonyls in the presence of aluminum alkyls. For example, the benzophenone-trimethylaluminum complexundergoes an irreversible fist order addition across the CO bond (eq. 2) with a half life of 48 minutes at 25°C.[23,24]

$$(C_6H_5)_2COAl(CH_3)_3 \rightarrow (C_6H_5)_2C(CH_3)OAl(CH_3)_2 \qquad (2)$$

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(17) Y. Okaya, M.S. Ahmed, R. Pepinsky, and V. Vand, *Z. Krist.*, *109*, 367 (1957).

(18) S.R. Rasmusse nand N.C. Broch, *Acta Chem. Scand.*, *20*, 1351 (1966).

(19) Distances and standard deviations, (   ), from the least squares plane as defined by W.C. Hamilton (*Acta Cryst.*, *14*, 185 (1961)) are Fe 0.000(3), C_b -0.001(2), O_b 0.003(1), and Al -0.001(10) Å.

(20) R.F. Bryan, P.T. Greene, M.J. Newlands, and David S. Field, *J. Chem. Soc.*, *A*, 3068 (1970).

(21) R.F. Bryan and P.T. Greene, *ibid.*, 3064 (1970).

(22) No difference in the Fe-Fe distance for the adduct is obtained when a riding model for thermal motion is assumed.

(23) E.C. Ashby, J. Laemmle, and H.M. Neumann, *J. Amer. Chem. Soc.*, *90*, 5179 (1968).

(24) Since completion of this manuscript on Al-OC distance of 1.83 Å has been reputed for $Al[W(CO)_3C_5H_5]_3(C_4H_8O)_3$: R.B. Peterson, J.J. Stezowski, C. Wan, J. Burlitch and R.E. Hughes, *J. Amer. Chem. Soc.*, *93*, 3532 (1971).