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Complexes of Polypyrazolylborate Ligands. V.* Characterization of Acetyl(tri-1-pyrazolylborato)(dicarbonyl)-Iron, $(HBpz_3)(COCH_3)(CO)_2Fe$, in Solution and in the Crystal

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The reaction of diiron enneacarbonyl with potassium tris-1-pyrazolylborate in the presence of excess methyl iodide affords an 8% yield of the new compound acetyl(tri-1-pyrazolylborato)(dicarbonyl)iron, **1**, *in addition to a larger quantity of the previously characterized compound bis-(tri-1-pyrazolylborato)iron,* **2**. *Compound* **1** *has been unequivocally characterized by elemental analyses, molecular weight measurement, pmr spectrum, and X-ray crystallographic structure determination. The infrared spectrum of* **1** *in solution shows that conformers are present; these presumably differ in the rotational orientation of the acetyl group relative to the rest of the molecule. The principal crystallographic data are: space group $P2_1/c$; cell dimensions $a = 9.233(1)$, $b = 12.331(4)$, $c = 15.507(2)$ Å, $\beta = 109.64(1)°$, $V = 1662.7(6)$ Å^3; observed and calculated densities $\rho_o = 1.40$ gcm^{-3}, $\rho_c = 1.36$ gcm^{-3} for $Z = 4$. Least-squares refinement using 1804 counter data gave final conventional R factors of 0.035 and 0.040. The structure consists of well-separated monomeric units of $(HBpz_3)(COCH_3)(CO)_2Fe$. Although not required crystallographically, the molecules possess near mirror symmetry. The coordination of the Fe atom is slightly perturbed from an octahedral arrangement, owing primarily to the non-orthogonal N-Fe-N angles of 86.8° (av). The pyrazolylborate nitrogen atoms occupy three mutually* cis *positions and the two CO groups are* cis *to each other. The oxygen atom of the acetyl group lies over the bisector of the angle subtended at Fe by the carbonyl groups. The Fe-N bond distances are 1.992(4), 1.999(3), and 2.082(4) Å* (trans *to acetyl); the Fe-C distances are 1.758(6), 1.771(5), and 1.968(5) Å (acetyl).*

Introduction

The pyrazolylborate class of ligand introduced by S. Trofimenko[1] has been shown capable of bonding to transition metals in a number of ways. The tri-1-pyrazolylborato ligand ($HBpz_3$) is tridentate in $(HBpz_3)(NNC_5H_5)(CO)_2Mo$[2] and bidentate in $(HBpz_3)(C_5H_5)(CO)_2Mo$[3]. Recently compounds of the type $(HBpz_3)(CO)_2XRu$ have been reported and in these the $HBpz_3$ ligand was shown to be tridentate. However in the same paper a compound which was said to analyse as $(HBpz_3)(CH_3)(CO)_2Fe$, was also briefly described. The infrared spectrum of this compound was said to have four bands in the carbonyl region instead of the expected two. In previous papers in this series,[3,5-8] we have been particularly concerned with elucidating such observations. Conformational non-rigidity of the pyrazolylborate ligand has been shown to be a general source of multiplicity of CO stretching bands in the infrared spectrum. However, in this case, the presence of a tridentate trispyrazolyl ligand would seem likely. Since such a structural element ought to be quite rigid, another explanation, probably involving some unrecognized structural feature of this molecule seemed likely to be involved.

We have conducted a careful investigation of this substance, leading to a reformulation of it and a sitasfactory explanation of its spectroscopic properties.

Experimental Section

Diiron enneacarbonyl, 0.91 gm (0.0025 moles), 1.26 gm (0.005 moles) of $KHBpz_3$ and 0.4 ml (excess) of CH_3I were refluxed gently under N_2 in 40 ml of THF for one hour. During this time the suspension turned brown, a gas was evolved and a dense white precipitate formed.

The solvent was stripped and the residue extracted with 40 ml of benzene. The reddish solution was filtered and the solvent stripped. All of these operations were carired out under nitrogen. The residue

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* For Part IV, see Ref. 8.

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[1] S. Trofimenko, *Accounts Chem. Research*, *4*, 17 (1971).

[2] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, *27*, 725 (1971).

[3] J.L. Calderon, F.A. Cotton, and A. Shaver, *J. Organometal. Chem.*, *37*, 127 (1972).

[4] M.I. Bruce, D.N. Sharrocks, and F.G.A. Stone, *J. Organometal. Chem.*, *31*, 269 (1971).

[5] J.L. Calderon, F.A. Cotton, and A. Shaver, *J. Organometal. Chem.*, *38*, 105 (1972).

[6] J.L. Calderon, F.A. Cotton, M. Jeremic, and A. Shaver, *Chem. Comm.*, 777 (1972).

[7] J.L. Calderon, F.A. Cotton, and A. Shaver, *J. Organometal. Chem.*, In Press.

[8] F.A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, *6*, 543 (1972).

was chromatographed on Woelm Alumina (Activity III) in benzene. Elution with benzene yielded a purple band identified as $(HBpz_3)_2Fe$ from its ultraviolet spectrum (yield, 0.413 g). Continued elution yielded 0.13 g (8%) of a bright yellow compound. The compound gave well-formed crystals by cooling a solution in 1:1, CH_2Cl_2-hexane.

Anal. Calcd for $C_{12}H_{13}BN_6O_2Fe[(HBpz_3)(CH_3)(CO)_2Fe]$, M.W., 339.94; C, 42.40; N, 24.73; H, 3.85. Calcd for $C_{13}H_{13}BN_6O_3Fe[(HBpz_3)(COCH_3)(CO)_2Fe]$ M.W., 367.95; C, 42.43; N, 22.85; H, 3.56. Found: M.W., by vapor phase osmometry: 372 (benzene), 371 ($CHCl_3$); C, 42.0; N, 24.1; H, 3.54.

Infrared spectra were recorded using a Perkin-Elmer Model 337 grating infrared spectrophotometer equipped with a scale expander, and 1.0 mm path-length sodium chloride cavity cells. The spectra were calibrated with indene. Variable temperature proton magnetic resonance spectra were recorded with a Varian HA-100 spectrometer equipped with a variable-temperature probe. Chemical shifts were calibrated by internal referencing with TMS. The temperature was measured with an uncalibrated Digitec Digital Thermocouple Thermometer (C-C type T). Analyses were performed by Meade Microanalytical Laboratories, Amherst, Mass.

Collection of X-ray Data. A golden-yellow crystal of dimensions 0.16×0.21×0.22 mm, with faces 110, $1\bar{1}0$, 001 and their respective Friedel pairs, was examined on a Syntex $P\bar{1}$ computer-controlled 4-circle diffractometer equipped with a graphite-crystal incident-beam monochromator. The operation of the diffractometer has been described previously.[9] A width at half-height of 0.32° was measured from ω scans of several strong reflections. Preliminary examination of the crystal on the diffractometer suggested that it belonged to the monoclinic system. Cell constants and the calculated volume derived from least-squares refinement of the setting angles for 15 reflections in the range $17° < 2\theta(\text{Mo K}\alpha) < 32°$ are: $a = 9.233(1)$, $b = 12.331(4)$, $c = 15.507(2)$ Å, $\beta = 109.64(1)°$, $V = 1662.7(6)$ Å^3. The calculated density is 1.36 gcm^{-3} for $Z = 4$ and mol. wt. = 339.93. This is in reasonable agreement with the observed density of 1.40 gcm^{-3} measured by flotation in aqueous cesium bromide.

The data were collected at 24° with Mo Kα radiation using the θ-2θ scan technique with a variable scan rate from 1.5 to 24.0°/min and a symmetric scan range from $2\theta(\text{Mo K}\alpha_1) - 0.9°$ to $2\theta(\text{Mo K}\alpha_2) + 0.9°$. An initial data set of 1198 independent reflections in the range $0° < 2\theta \leqslant 35°$ was collected. This was later followed by collection of 1569 independent reflections in the range $35° < 2\theta \leqslant 48°$.

Three representative reflections were selected as standards, and their intensities were measured preiodically as a check on crystal and electronic stability. For the initial data set these reflections showed no significant decrease in intensity when compared to the standard deviations on the intensities based on counting statistics alone. However in the second data set the three standards fell in intensity to 81%, 73%, and 70% of their original values, respectively. The non-uniform loss in intensity was approximately corrected for with a linear function and an average loss of 0.016% per reflection collected. As will be noted later, this correction was not entirely satisfactory.

Of the 2767 reflections in the range $0° < 2\theta < 48°$, 1804 reflections had $F_o^2 > 3\sigma(F_o^2)$. Lorentz and polarization corrections were applied[10] to the data. For Mo Kα radiation the linear absorption coefficient of the compound is 9.45 cm^{-1}. Preliminary calculations[10] showed transmission factors varying only from 83% to 87%; hence a correction was not applied. No evidence of secondary extinction was found in a survey of observed and calculated structure factors.

Solution of the Structure. Examination of the data showed the following conditions limiting the observation of reflections: $hk\ell$, no conditions; $h0\ell$, $\ell = 2n$; $0k0$, $k = 2n$. Refinement was therefore carried out in space group $P2_1/c$ of the monoclinic system. The position of the Fe atom was located from a three-dimensional Patterson synthesis.[10] The positional paramenters and a scale factor were varied in one cycle of full-matrix least-squares refinement,[10] giving agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.43$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.45$. This was followed by a difference Fourier synthesis[10] which revealed the positions of fifteen other atoms. The remaining non-hydrogen atoms were located from a succeeding difference Fourier map.

The quantity minimized in least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were calculated using a computer program by Cromer. Anomalous dispersion effects for Fe were included in calculations of F_c;[11] the values of Δf′ and Δf″ were taken from Cromer and Liberman.[12]

A earlier report[4] of the compound had suggested the composition $(HBpz_3)(CH_3)(CO)_2Fe$. It was evident from least-squares refinements and difference Fourier maps that the molecule in the crystal did not include a methyl group bonded to the Fe atom. The geometry of the ligand in the Fourier map and successful least-squares refinement identified the supposed methyl ligand as an acetyl group. This identification was later shown to be consistent with the nmr and ir spectra and elemental analysis (*vide infra*).

Full-matrix least-squares refinement (218 variables) of the 24 non hydrogen atoms, including anisotropic

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(9) F.A. Cotton, B.A. Frenz, G. Deganellò, and A. Shaver, *J. Organometal. Chem.*, In Press.

(10) *The following computer programs written for the IBM 360* were used: DATARED, a data reduction program by Frenz; AGNOST, an absorption correction program by Cahen based Coppens' DATAPP and Tompa analytical subroutines of Cullen's program; JIMDAP, a version of Zalkin's FORDAP Fourier program modified by Ibers; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program; SADIAN, a program for calculating atomic distances and angles by Baur; RSCAN, a structure factor analysis program by Doedens; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

(11) J.A. Ibers and W.C. Hamilton, *Acta Crystallogr.*, *17*, 781 (1964).

(12) D.T. Cromer and D. Liberman, *J. Chem. Phys.*, *53*, 1891 (1970).

Table I. Values (in electrons) for $10|F_o|$ and $10|F_c|$ for $(HBpz_3)(COCH_3)(CO)_2Fe$.

K	L	FOBS	FCALC
H= 0			
0	2	1951	1971
0	4	423	410
0	6	305	291
0	8	142	154
0	10	498	496
0	12	403	393
0	14	222	220
0	16	140	141
1	-16	173	172
1	-11	118	130
1	-10	251	292
1	-9	147	141
1	-8	85	111
1	-7	129	113
1	-6	140	112
1	-5	589	576
1	-4	569	570
1	-3	447	456
1	-2	877	872
1	2	880	872
1	3	442	456
1	4	578	570
1	5	594	576
1	6	137	112
1	7	122	113
1	8	91	111
1	9	149	141
1	10	253	252
1	11	126	130
1	14	86	68
1	16	158	172
2	-14	133	131
2	-13	149	147
2	-12	334	323
2	-11	305	296
2	-10	322	321
2	-9	155	151
2	-7	329	328
2	-5	462	452
2	-4	478	455
2	-2	599	585
2	-1	778	767
2	0	1769	1742
2	1	786	767
2	2	607	585
2	4	689	655
2	5	450	452
2	7	328	328
2	9	157	151
2	10	326	321
2	11	301	296
2	12	330	323
2	13	138	167
2	14	139	131
3	-16	118	119
3	-14	88	102
3	-12	83	96
3	-11	325	316
3	-10	322	317
3	-9	483	479
3	-8	321	327
3	-7	575	576
3	-6	201	208
3	-5	501	487
3	-4	573	558
3	-3	583	570
3	-2	1469	1437
3	-1	247	244
3	1	247	243
3	2	1471	1437
3	3	590	570
3	4	575	558
3	5	493	487
3	6	197	208
3	7	566	574
3	8	312	323
3	9	480	479
3	10	322	317
3	11	316	316
3	12	83	96
3	14	103	102
3	16	125	119
4	-13	232	231
4	-11	485	481
4	-9	450	454
4	-8	220	210
4	-7	568	557
4	-6	152	140
4	-5	140	148
4	-4	640	612
4	-3	615	610
4	-2	289	275
4	-1	895	880
4	0	830	798
4	1	890	880
4	2	287	275
4	3	610	610
4	4	648	612
4	5	145	148
4	6	149	140
4	7	558	557
4	8	209	210
4	9	454	454
4	11	478	481
4	13	233	231
5	-15	89	89
5	-11	153	157
5	-10	169	173
5	-9	363	356
5	-8	138	124
5	-7	384	380
5	-5	307	307
5	-4	352	342
5	-3	114	127
5	-2	668	654
5	-1	477	459
5	1	467	458
5	2	656	654
5	3	118	127
5	4	340	342
5	5	306	307
5	7	370	380
5	8	136	124
5	9	363	356
5	10	185	173
5	11	156	157
6	-15	180	183
6	-13	219	210
6	-12	104	88
6	-11	295	286
6	-10	94	87
6	-9	234	236
6	-8	151	151
6	-7	121	125
6	-5	333	332
6	-4	316	324
6	-3	244	242
6	-2	470	461
6	-1	423	439
6	0	333	323
6	1	633	639
6	2	473	461
6	3	240	242
6	4	321	324
6	5	332	332
6	7	128	125
6	8	144	151
6	9	235	236
6	10	65	67
6	11	271	286
6	12	95	98
6	13	208	210
6	15	166	183
7	-14	137	142
7	-13	110	108
7	-11	85	78
7	-10	147	146
7	-9	176	173
7	-8	182	190
7	-7	291	287
7	-6	349	352
7	-5	444	447
7	-3	108	111
7	-2	425	422
7	-1	188	184
7	1	194	184
7	2	427	422
7	3	110	111
7	5	467	447
7	6	351	352
7	7	291	287
7	8	183	190
7	9	171	173
7	10	137	146
7	11	79	78
7	13	107	108
7	14	117	142
8	-13	147	125
8	-12	113	119
8	-11	137	129
8	-10	88	80
8	-8	170	181
8	-7	108	97
8	-5	148	148
8	-4	337	349
8	-3	239	235
8	-2	334	341
8	-1	137	134
8	0	161	160
8	1	138	134
8	2	336	341
8	3	243	235
8	4	350	349
8	5	151	143
8	7	88	97
8	8	165	181
8	11	116	129
8	12	140	119
8	13	129	125
9	-10	192	185
9	-9	96	91
9	-8	181	172
9	-6	270	267
9	-5	141	132
9	-4	304	299
9	-3	140	134
9	-2	216	214
9	-1	155	160
9	1	160	160
9	2	230	214
9	3	132	134
9	4	313	299
9	5	139	132
9	6	265	267
9	8	170	172
9	9	91	91
9	10	177	185
10	-11	100	101
10	-10	121	120
10	-8	113	103
10	-5	75	52
10	-4	201	196
10	-2	224	220
10	-1	118	108
10	0	237	231
10	1	108	108
10	2	225	220
10	4	206	196
10	8	93	103
10	10	109	120
10	11	72	101
11	-10	94	102
11	10	105	102
13	5	82	86
14	-1	185	190
14	0	89	93
14	1	179	190
H= 1			
0	-16	110	108
0	-12	133	141
0	-10	437	422
0	-8	206	220
0	-6	131	127
0	-2	543	597
0	0	522	515
0	2	343	343
0	4	186	176
0	6	456	439
0	8	166	163
0	10	190	191
0	12	216	224
0	14	242	241
0	16	126	120
1	-17	75	65
1	-16	173	184
1	-15	100	116
1	-14	438	428
1	-13	204	216
1	-12	403	405
1	-11	136	130
1	-10	132	135
1	-9	206	196
1	-8	229	232
1	-7	126	122
1	-6	107	120
1	-5	361	353
1	-4	1160	1135
1	-3	319	320
1	-2	1523	1521
1	-1	196	193
1	0	1806	1899
1	1	310	317
1	2	469	485
1	3	234	250
1	4	441	431
1	5	226	219
1	6	416	393
1	8	587	594
1	9	107	119
1	10	386	387
1	11	86	86
1	12	342	359
1	14	83	75
2	-16	77	86
2	-13	81	70
2	-12	136	147
2	-11	123	128
2	-10	273	276
2	-9	319	322
2	-8	177	185
2	-7	391	408
2	-6	630	626
2	-5	413	419
2	-4	893	892
2	-3	180	179
2	-2	246	250
2	-1	273	251
2	1	752	751
2	2	893	878
2	3	1062	1065
2	4	616	609
2	5	466	474
2	6	673	497
2	7	259	244
2	9	294	290
2	10	126	108
2	11	165	160
2	12	129	137
2	13	94	80
2	14	188	199
2	15	111	119
3	-15	209	186
3	-14	222	212
3	-13	317	304
3	-12	232	231
3	-11	438	434
3	-9	377	390
3	-8	223	221
3	-7	275	262
3	-6	149	164
3	-5	450	452
3	-4	252	247
3	-3	503	491
3	-2	745	707
3	-1	263	256
3	0	271	264
3	1	998	957
3	2	558	529
3	3	155	159
3	5	255	258
3	6	132	116
3	7	436	436
3	8	100	109
3	9	132	139
3	10	198	209
3	11	146	148
3	12	148	164
4	-16	110	110
4	-12	356	311
4	-11	282	274
4	-10	458	450
4	-9	486	488
4	-8	198	149
4	-7	166	189
4	-6	218	227
4	-5	220	239
4	-4	224	231
4	-2	166	194
4	-1	142	148
4	0	247	236
4	1	881	844
4	2	405	388
4	3	509	503
4	4	405	375
4	5	601	616
4	6	598	585
4	7	434	429
4	8	286	296
4	9	173	142
4	11	125	133
4	12	227	257
4	13	149	150
4	15	176	183
5	-16	93	79
5	-15	144	137
5	-13	348	328
5	-11	545	347
5	-9	97	92
5	-7	319	325
5	-6	507	488
5	-5	214	230
5	-4	322	298
5	-3	368	373
5	-2	118	108
5	-1	805	800
5	1	674	654
5	2	196	189
5	3	186	187
5	4	214	209
5	5	265	248
5	7	303	314
5	8	116	111
5	9	248	238
5	10	81	77
5	11	263	284
5	13	184	194
5	15	84	57
6	-15	85	83
6	-13	90	92
6	-12	118	126
6	-9	371	376
6	-8	116	107
6	-7	391	405
6	-6	93	93
6	-5	305	314
6	0	135	147
6	1	565	562
6	3	445	444
6	5	564	560
6	6	134	129
6	7	297	297
6	8	193	179
6	13	122	119
6	14	106	114
7	-15	85	95
7	-13	86	76
7	-12	166	175
7	-11	201	193
7	-10	152	142
7	-8	96	83
7	-7	175	167
7	-5	290	292
7	-4	306	301
7	-3	440	438
7	-2	423	412
7	-1	564	574
7	0	284	285
7	1	485	502
7	5	109	119
7	7	181	176
7	9	128	125
7	11	118	110
7	12	78	61
7	13	193	202
8	-12	86	88
8	-10	138	141
8	-9	167	141
8	-8	268	257
8	-6	458	461
8	-5	196	187
8	-4	159	152
8	-3	157	164
8	0	253	238
8	1	287	289
8	2	436	427
8	3	223	228
8	4	395	400
8	5	247	238
8	6	253	244
8	7	128	119
8	8	92	85
8	11	76	69
8	12	78	64
8	13	89	92
9	-13	84	59
9	-12	143	136
9	-11	157	144
9	-10	166	164
9	-8	98	110
9	-7	123	127
9	-5	126	128
9	-4	166	159
9	-3	125	131
9	-2	163	166
9	-1	115	110
9	0	530	334
9	1	188	181
9	2	175	170
9	10	128	123
9	11	74	81
9	12	170	174
10	-10	230	244
10	-9	136	157
10	-8	223	226
10	-6	266	270
10	-5	101	98
10	-4	281	284
10	-3	114	119
10	0	294	298
10	2	260	291
10	4	134	136
10	6	272	268
10	8	142	155
11	-10	124	124
11	0	70	172
12	-8	172	160
12	7	85	83
12	8	79	30
13	-5	88	87
13	-4	129	123
13	3	94	122
H= 2			
0	-16	216	217
0	-14	291	279
0	-12	365	367
0	-10	119	108
0	-8	336	321
0	-6	771	765
0	-4	1067	1069
0	-2	632	648
0	0	725	693
0	6	367	377
0	8	282	294
0	10	162	164
0	12	411	418
1	-12	165	154
1	-11	62	72
1	-10	444	435
1	-8	430	455
1	-7	232	242
1	-6	556	579
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1	-3	178	176
1	-2	640	627
1	-1	136	135
1	0	384	398
1	1	144	143
1	3	103	96
1	6	101	88
1	8	367	362
1	9	77	85
1	10	284	281
2	-14	169	159
2	-12	176	162
2	-11	170	174
2	-10	360	356
2	-9	350	350
2	-8	474	465
2	-7	205	222
2	-6	179	182
2	-4	267	266
2	-3	225	211
2	-2	267	245
2	-1	309	306
2	0	477	468
2	1	174	170
2	2	268	267
2	3	227	221
2	6	131	149
2	8	156	148
3	-16	110	97
3	-15	278	266
3	-14	199	201
3	-13	277	272
3	-11	102	101
3	-8	238	243
3	-6	121	129
3	-5	260	258
3	-4	136	145
3	-3	501	495
3	-2	216	233
3	-1	237	213
3	0	156	159
3	1	284	282
3	3	201	209
3	5	92	90
3	7	204	215
3	9	187	193
4	-14	76	82
4	-13	230	259
4	-11	183	177
4	-9	306	309
4	-8	143	145
4	-7	282	288
4	-3	249	261
4	-2	193	181
4	-1	348	347
4	0	197	189
4	1	296	303
4	2	255	254
4	4	152	156
4	5	94	108
4	6	117	124
5	-15	254	244
5	-13	86	82
5	-12	112	101
5	-10	196	194
5	-7	169	169
5	-5	216	208
5	-3	378	382
5	-2	94	95
5	-1	352	360
5	1	319	318
5	2	173	174
5	5	180	182
5	6	222	244
5	7	208	218
5	8	86	96
5	9	198	222
6	-15	105	93
6	-13	182	191
6	-11	147	154
6	-9	362	358
6	-8	85	88
6	-7	482	481
6	-6	265	248
6	-5	317	324
6	-4	185	186
6	-2	106	113
6	-1	148	132
6	1	148	140
6	2	74	75
6	3	227	227
6	4	144	126
6	5	156	162
6	7	86	92
7	-13	86	89
7	-7	196	201
7	-5	231	228
7	-4	101	103
7	-3	308	297
7	-2	223	227
7	-1	75	52
7	0	139	135
7	3	97	101
7	7	132	156
8	-13	174	184
8	-12	132	157
8	-10	214	207
8	-9	130	138
8	-8	206	216
8	-7	190	190
8	-6	213	212
8	-5	214	231
8	-2	219	216
8	0	147	149
8	2	136	140
8	3	120	128
8	4	233	223
8	5	140	147
9	-5	83	73
9	-4	171	166
9	-3	84	98
9	-2	196	187
9	0	160	157
9	2	222	219
9	5	98	96
10	-10	89	82
10	-8	130	123
10	-7	84	61
10	-6	109	99
10	-2	117	127
10	0	208	189
10	2	220	215
11	-7	136	128
11	-6	119	109
11	-4	179	184
11	-2	289	213
11	0	141	146
H= 7			
0	-16	103	105
0	-14	276	266
0	-12	103	113
0	-8	374	370
0	-6	629	626
0	-4	665	641
0	-2	565	565
0	2	184	176
0	4	205	199
0	6	215	206
0	8	263	264
1	-14	259	255
1	-12	331	328
1	-11	106	34
1	-10	79	80
1	-9	87	77
1	-8	272	280
1	-7	89	111
1	-6	221	228
1	-5	216	217
1	-4	234	242
1	-3	82	84
1	3	98	86
1	6	94	97
1	7	76	89
2	-16	161	158
2	-15	198	207
2	-14	193	192
2	-13	318	331
2	-12	122	117
2	-11	197	189
2	-10	77	72
2	2	154	146
2	4	214	213
2	5	197	143
2	6	134	124
2	7	84	86
2	8	161	159
3	-15	119	117
3	-14	127	133
3	-13	215	213
3	-12	199	201
3	-9	104	95
3	1	201	182
3	2	135	121
3	3	211	195
3	5	105	111
3	8	73	24
4	-15	273	274
4	-14	85	85
4	-13	294	299
4	-11	123	121
4	-8	83	90
4	-7	339	341
4	-1	316	326
4	0	80	83
4	2	241	234
4	3	89	90
4	5	184	179
4	6	96	108
4	7	159	143
5	-15	79	67
5	-13	231	239
5	-11	275	287
5	-9	312	309
5	-5	130	140
5	-2	157	173
5	-1	202	291
5	0	154	159
5	1	294	267
5	2	92	104
5	3	222	230
5	5	97	104
5	6	70	47
6	-14	94	82
6	-13	119	106
6	-12	128	131
6	-8	237	245
6	-7	188	191
6	-6	168	186
6	-5	163	146
6	-3	365	363
6	-1	122	118
6	0	92	90
6	1	99	115
6	4	87	110
6	5	119	116
6	6	101	120
7	-13	149	169
7	-12	107	102
7	-11	223	242
7	-10	151	154
7	-9	291	253
7	-7	100	84
7	-1	181	176
7	1	168	163
7	2	131	133
7	3	184	197
7	4	92	107
7	5	121	136
8	-12	81	88
8	-9	121	107
8	-7	162	181
8	-6	147	136
8	-4	253	256
8	-2	204	197
8	0	93	89
8	2	88	100
9	-10	221	229
9	-8	125	116
9	-6	75	76
9	-4	130	134
9	-2	145	149
9	-1	114	112
9	0	112	106
9	2	120	117
10	-8	159	163
10	-6	177	146
10	-5	119	113
10	-4	124	118
10	-2	185	168
10	0	149	133
H= 8			
0	-14	280	281
0	-12	399	417
0	-10	231	224
0	-8	118	123
0	-6	82	77
0	-2	216	213
0	0	252	250
0	2	251	245
0	4	301	274
1	-15	120	105
1	-14	140	148
1	-13	126	129
1	-10	206	201
1	-9	86	44
1	-8	143	145
1	-7	211	202
1	-6	307	302
1	-5	234	237
1	-4	319	312
1	-3	168	171
1	-2	151	134
1	-1	92	60
1	0	229	220
1	2	131	136
1	3	101	88
1	4	279	260
1	6	235	212
2	-14	252	252
2	-13	105	89
2	-12	298	298
2	-11	68	35
2	-9	104	88
2	-8	123	123
2	-7	151	153
2	-6	87	93
2	-5	167	170
2	-4	111	114
2	-2	230	217
2	-1	81	74
2	0	117	104
2	1	141	139
2	2	137	153
2	3	157	144
2	4	203	191
3	-14	95	77
3	-13	198	203
3	-10	115	116
3	-9	194	200
3	-7	327	340
3	-6	181	188
3	-5	317	326
3	-4	233	229
3	-3	328	307
3	-2	145	139
3	-1	170	152
3	1	75	62
3	3	109	103
3	4	190	179
4	-13	185	189
4	-12	132	108
4	-11	151	141
4	-9	74	74
4	-6	75	55
4	-5	190	175
4	-3	157	203
4	-2	176	185
4	-1	353	333
4	0	152	168
4	1	267	256
4	2	75	60
4	3	166	161
5	-12	66	61
5	-9	124	125
5	-8	143	132
5	-7	246	245
5	-5	216	219
5	-3	266	292
5	-1	124	118
5	1	100	110
5	2	149	138
5	3	107	117
6	-11	299	297
6	-10	89	80
6	-9	134	117
6	-3	97	80
6	-1	327	344
6	0	87	63
6	1	194	205
6	3	56	110
7	-11	97	96
7	-9	181	179
7	-8	140	143
7	-7	250	254
7	-6	222	231
7	-5	132	115
7	-4	126	127
7	-3	75	51
8	-10	164	163
8	-9	66	97
8	-6	55	107
8	-4	132	123
8	-2	118	117
8	-1	150	133
8	0	118	129
8	1	87	89
9	-6	162	176
9	-4	77	73
9	-3	91	71
9	-2	81	92
H= 9			
0	-12	93	94
0	-10	322	324
0	-8	291	302
0	-4	164	197
0	2	121	108
1	-13	109	92
1	-12	337	345
1	-10	314	303
1	-9	73	69
1	-6	183	187
1	-4	133	133
1	-2	204	183
1	0	341	353
1	1	73	75
1	2	241	231
2	-11	153	157
2	-10	232	209
2	-9	171	178
2	-8	225	227
2	-7	254	253
2	-6	121	128
2	-5	155	151
2	0	60	58
2	1	106	89
2	2	176	161
2	3	81	68
3	-13	112	104
3	-11	124	127
3	-10	121	99
3	-9	137	133
3	-6	212	213
3	-5	123	142
3	-4	90	107
3	-3	159	155
3	-1	274	261
3	0	176	179
3	1	197	163
3	2	46	77
4	-11	215	222
4	-10	134	146
4	-9	134	147
4	-6	197	196
4	-7	141	142
4	-5	143	147
4	-3	123	98
4	-2	119	119
4	1	115	126
5	-11	226	223
5	-9	113	105
5	-8	138	139
5	-6	143	130
5	-5	110	124
5	-3	264	251
5	-1	301	303
5	1	152	143
6	-9	185	178
6	-7	157	168
6	-6	82	64
6	-5	104	110
6	-4	96	83
6	0	99	65
7	-8	117	134
7	-5	66	64
7	-4	125	124
7	-3	112	122
7	-2	182	186
H= 10			
0	-10	152	144
0	-6	142	142
0	-4	236	245
0	-2	250	229
1	-11	104	111
1	-10	288	291
1	-9	133	136
1	-8	256	241
1	-6	78	43
2	-10	121	136
2	-6	191	198
2	-4	159	144
2	-3	130	111
2	-2	117	113
2	-1	139	144
3	-9	171	170
3	-8	211	214
3	-7	111	131
3	-6	117	123
4	-8	108	106
4	-6	115	137
4	-5	158	179
4	-3	196	214

Table II. Positional and Anisotropic Thermal Parameters and Their Standard Deviations for the Non-hydrogen Atoms.[a]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	0.18735(7)	0.29960(5)	0.20900(4)	86(1)	62(1)	35(1)	9(1)	26(1)	0(1)
O(4)	0.0682(6)	0.5003(4)	0.1133(3)	278(9)	118(4)	87(3)	102(5)	82(4)	44(3)
O(5)	0.0098(5)	0.3312(4)	0.3305(3)	253(8)	161(5)	81(2)	51(5)	109(4)	10(3)
O(6)	—0.1221(5)	0.2522(5)	0.1086(5)	95(6)	223(7)	166(5)	4(5)	28(4)	—91(5)
C(4)	0.1151(6)	0.4212(5)	0.1514(3)	142(7)	89(5)	44(2)	45(5)	42(3)	13(3)
C(5)	0.0799(6)	0.3192(4)	0.2833(3)	133(7)	81(5)	51(2)	22(5)	41(4)	5(3)
C(6)	0.0080(5)	0.2246(5)	0.1239(3)	90(6)	108(6)	59(3)	—3(4)	31(3)	—11(3)
C(7)	0.0334(8)	0.1229(6)	0.0753(5)	136(8)	122(7)	67(4)	—27(6)	20(5)	—28(4)
B	0.5245(5)	0.2085(4)	0.2623(3)	97(6)	51(4)	40(2)	7(4)	26(3)	—1(3)
Pyrazolylborate ring R1:									
N(1)	0.3093(4)	0.2766(3)	0.1257(2)	93(5)	64(3)	31(2)	10(3)	24(2)	0(2)
N(2)	0.4549(4)	0.2368(3)	0.1597(2)	89(5)	50(3)	36(2)	—1(3)	29(2)	—2(2)
C(1)	0.5176(6)	0.2356(4)	0.0926(3)	135(7)	53(4)	48(2)	—4(4)	46(3)	—4(2)
C(2)	0.4123(6)	0.2748(4)	0.0144(3)	166(8)	76(4)	42(2)	0(4)	46(3)	0(2)
C(3)	0.2837(6)	0.2999(5)	0.0378(3)	147(7)	79(4)	37(2)	2(5)	35(3)	—1(3)
Pyrazolylborate ring R2:									
N(1)	0.3876(4)	0.3661(3)	0.3002(2)	120(5)	49(3)	34(2)	0(3)	26(2)	0(2)
N(2)	0.5234(4)	0.3138(3)	0.3152(2)	81(4)	59(3)	35(2)	2(3)	17(2)	0(2)
C(1)	0.6365(6)	0.3685(4)	0.3788(3)	125(6)	81(4)	39(2)	—23(5)	20(3)	—4(3)
C(2)	0.5743(7)	0.4573(5)	0.4063(3)	198(10)	69(4)	44(2)	—27(5)	36(4)	—11(3)
C(3)	0.4286(6)	0.4529(4)	0.3557(3)	167(8)	52(4)	45(2)	—9(4)	46(4)	—5(2)
Pyrazolylborate ring R3:									
N(1)	0.2665(4)	0.1584(3)	0.2687(2)	101(5)	53(3)	39(2)	—3(3)	28(2)	0(2)
N(2)	0.4155(4)	0.1293(3)	0.2860(2)	122(5)	44(3)	39(2)	12(3)	31(2)	0(2)
C(1)	0.4411(7)	0.0320(4)	0.3283(4)	189(9)	59(4)	51(3)	23(5)	48(4)	5(3)
C(2)	0.3084(7)	—0.0023(5)	0.3393(4)	242(11)	52(4)	74(3)	—3(6)	82(5)	7(3)
C(3)	0.2025(6)	0.0777(4)	0.3016(3)	158(8)	66(4)	56(3)	—18(5)	51(4)	0(3)

[a] Parameters x, y, and z refer to fractional coordinates. The anisotropic temperature factor is in the form of $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+\beta_{12}hk+2\beta_{13}h\ell+2\beta_{23}k\ell)]$. Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Positional Parameters and their Standard Deviations for Hydrogen Atoms.

Atom[a]	x	y	z
H(on B)	0.652(9)	0.173(6)	0.281(5)
Methyl group:			
H(7,1)	0.139(10)	0.098(6)	0.101(5)
H(7,2)	—0.052(10)	0.077(6)	0.060(5)
H(7,3)	0.031(9)	0.147(6)	0.014(6)
Pyrazolylborate ring R1:			
H(1)	0.625(9)	0.203(6)	0.111(5)
H(2)	0.433(8)	0.287(6)	—0.041(5)
H(3)	0.180(9)	0.334(6)	0.002(5)
Pyrazolylborate ring R2:			
H(1)	0.742(9)	0.340(6)	0.395(5)
H(2)	0.635(9)	0.507(6)	0.455(5)
H(3)	0.333(9)	0.504(6)	0.356(5)
Pyrazolylborate ring R3:			
H(1)	0.544(10)	0.001(6)	0.345(5)
H(2)	0.293(9)	—0.066(7)	0.363(5)
H(3)	0.098(10)	0.088(6)	0.297(5)

[a] Hydrogen are numbered according to the carbon atoms to which they are bonded.

Table IV. Root-mean-square Amplitudes of Vibration (Å).

Atom	Min	Intermed	Max
Fe	0.162(1)	0.198(1)	0.223(1)
O(4)	0.205(6)	0.265(5)	0.406(6)
O(5)	0.176(5)	0.318(5)	0.384(5)
O(6)	0.189(6)	0.304(6)	0.523(7)
C(4)	0.180(7)	0.205(7)	0.298(7)
C(5)	0.193(7)	0.231(6)	0.267(1)
C(6)	0.178(7)	0.242(6)	0.297(7)
C(7)	0.206(8)	0.266(7)	0.335(8)
B	0.176(7)	0.205(7)	0.209(6)
Pyrazolylborate ring R1:			
N(1)	0.165(5)	0.192(5)	0.226(5)
N(2)	0.162(5)	0.192(5)	0.209(5)
C(1)	0.181(6)	0.200(7)	0.250(6)
C(2)	0.183(6)	0.242(7)	0.257(6)
C(3)	0.187(6)	0.239(6)	0.247(6)
Pyrazolylborate ring R2:			
N(1)	0.183(5)	0.195(6)	0.215(5)
N(2)	0.176(5)	0.195(4)	0.214(5)
C(1)	0.196(7)	0.215(6)	0.265(7)
C(2)	0.199(7)	0.228(6)	0.288(7)
C(3)	0.192(7)	0.201(7)	0.261(6)
Pyrazolylborate ring R3:			
N(1)	0.182(5)	0.202(5)	0.211(5)
N(2)	0.172(6)	0.196(5)	0.225(5)
C(1)	0.199(7)	0.217(6)	0.281(7)
C(2)	0.190(8)	0.232(7)	0.324(7)
C(3)	0.189(7)	0.233(7)	0.268(6)

temperature factors, gave agreement factors R_1 = 0.050 and R_2 = 0.053. The positions of the thirteen hydrogen atoms were readily ascertained in a difference Fourier synthesis. With the hydrogen isotropic temperature factor fixed at 6 A^2, the hydrogen atomic positions were refined along with the remainder of the structure. All atoms bonded to hydrogen atoms shifted away from the hydrogen atoms to which they are attached by *ca.* 0.02 Å, the largest shift being 2.6 times the standard deviation of the parameter. The final R factors are 0.035 and 0.040. A thorough examination[10] of observed and calculated structure factors as a function of Miller indices, λ^{-1} sinθ, the mangitude of F_o, etc. revealed no significant trends in the first data set. However, the second data set showed increased discrepancies in R values as a function of the number of data collected. It was conluded that the poor agreement was a result of inadequate correction for the loss of intensity observed in the standards. A cycle of least-squares refinement using only the first data set and refining all atoms, with temperature factors on hydrogen atoms fixed at 6 A^2, gave R factors of 0.023 and 0.025. No parameter shifted by more than three times its standard deviation, hence the inadequate correction for decomposition does not introduce significant changes in the structure. For this reason it was felt that little could be gained by recollecting the data on another crystal. A list of $|F_o|$ and $|F_c|$ values for both data sets is given in Table I. In the final least-squares cycle no parameter shifted by more than twice its standard deviation. The error in an observation of unit weight is 1.34. A final difference Fourier synthesis revealed no residual electron density greater than 0.32 e A^{-3}, where hydrogen atoms in a previous map appeared at 0.41 e A^{-3}. In all tables of atomic parameters and molecular dimensions, values are derived from the final least-squares refinement based on the entire data set.

Positional and anisotropic thermal parameters for the non-hydrogen atoms are given in Table II. The refined positional parameters for the hydrogen atoms are listed in Table III. Table IV gives root-mean-square amplitudes of vibration for the non-hydrogen atoms.

Results

Preparation and Isolation. In this work it was shown that the title compound can be isolated in pure crystalline form without recourse to sublimation. The material isolated by crystallization from 1:1 CH_2Cl_2-hexane is the pure acetyl compound, $(HBpz_3)(COCH_3)(CO)_2Fe$.

Crystal and Molecular Structure. The structure of the molecule as it occurs in the crystal is shown in Fig. 1. The entire molecule constitutes the asymmetric unit and thus possesses no rigorous, crystallographic symmetry. However the molecule shows near mirror symmetry.

The iron atom is six-coordinate, with three mutually *cis* positions occupied by nitrogen atoms of the tri-1-pyrazolylborate ligand and the remaining three positions occupied by the two carbonyl groups and the acetyl group. The rotational orientation of the acetyl group in the crystalline compound is such that the acetyl oxygen atom lies near the bisector of the OC-Fe-CO angle and the methyl group lies near the bisector of the N-Fe-N angle formed by the two coordinated nitrogen atoms that are *trans* to the carbonyl

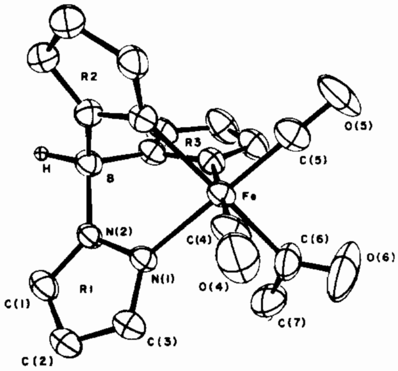

Figure 1. The molecular structure of $(HBpz_3)(COCH_3)(CO)_2$-Fe as found in the crystal. R1, R2, and R3 identify the three rings of the pyrazolylborate ligand and are referenced in the tables and the text. The 50% probability thermal ellipsoids are shown; the size of the ellipsoid for the hydrogen on the boron atom is arbitrarily reduced. For the sake of clarity, other hydrogen atoms are not shown.

Table V. Selected Bond Distances (Å)[a]

Atoms	R1	R3	R2	av[b]
Fe-N(1)	1.999(3)	2.082(4)	1.992(4)	2.024
N(1)-N(2)	1.360(4)	1.359(5)	1.359(5)	1.359(1)
N(2)-C(1)	1.350(5)	1.350(6)	1.350(6)	1.350(0)
C(1)-C(2)	1.362(7)	1.370(8)	1.360(8)	1.364(5)
C(2)-C(3)	1.388(7)	1.388(8)	1.374(8)	1.383(8)
C(3)-N(1)	1.334(5)	1.343(6)	1.342(6)	1.340(5)
N(2)-B	1.543(6)	1.538(6)	1.533(6)	1.538(5)

Atoms	Distance	Atoms	Distance
Fe-C(4)	1.758(6)	C(4)-O(4)	1.147(6)
Fe-C(5)	1.771(5)	C(5)-O(5)	1.139(5)
Fe-C(6)	1.968(5)	C(6)-O(6)	1.193(6)
Fe···B	3.147(5)	C(6)-C(7)	1.522(8)
B-H	1.19(8)		
C-H (pz)	0.98(4)[b] av		
C-H (methyl)	0.96(3)[b] av		

[a] R1, R2 and R3 refer to rings 1, 2, and 3 as designated in Fig. 1. [b] Numbers in parentheses are standard deviations from the average, although in all cases this is less than or equal to the standard deviation on an individual value. No standard deviation is given for the average Fe-N distance since this is an average of non-equivalent bonds. The standard deviation on each of the individual C-H bond distance is 0.08 Å.

Table VI. Selected Bond Angles (Deg.)[a].

Atoms	R1	R2	R3	av[b]
Fe-N(1)-N(2)	119.9(2)	119.2(3)	120.8(3)	120.0(8)
Fe-N(1)-C(3)	133.2(3)	134.3(3)	133.2(3)	133.6(6)
B-N(2)-N(1)	119.7(3)	118.7(3)	119.1(3)	119.2(5)
B-N(2)-C(1)	130.9(4)	132.0(4)	131.4(4)	131.4(6)
C(3)-N(1)-N(2)	106.6(3)	106.4(4)	106.0(4)	106.3(3)
N(1)-N(2)-C(1)	109.2(3)	109.3(4)	109.3(4)	109.3(1)
N(2)-C(1)-C(2)	108.6(4)	108.9(5)	108.7(5)	108.7(2)
C(1)-C(2)-C(3)	105.3(4)	104.8(4)	105.4(5)	105.2(3)
C(2)-C(3)-N(1)	110.2(4)	110.5(5)	110.7(5)	110.5(3)
N(2)-B-H	111(3)	111(3)	113(3)	112(1)
N(1)-Fe-C(4)	89.6(2)	96.2(2)	177.3(2)	—
N(1)-Fe-C(5)	179.6(2)	93.9(2)	90.9(2)	—
N(1)-Fe-C(6)	91.7(2)	175.0(2)	89.7(2)	—
Fe-N(1)-N(2)-B[c]	0.6(5)	1.3(4)	2.3(5)	1.4(9)
	R1-R2	R1-R3	R2-R3	av[b]
N(1)-Fe-N(1)	86.0(1)	88.7(1)	85.7(1)	86.8(17)
N(2)-B-N(2)	106.5(4)	108.2(3)	106.8(3)	107.2(9)

Atoms	Angle	Atoms	Angle
C(4)-Fe-C(5)	90.8(2)	Fe-C(4)-O(4)	179.6(4)
C(4)-Fe-C(6)	88.3(2)	Fe-C(5)-O(5)	179.4(5)
C(5)-Fe-C(6)	88.3(2)	Fe-C(6)-O(6)	124.3(4)
O(6)-C(6)-C(7)	116.7(5)	Fe-C(6)-C(7)	119.0(4)

[a] R1, R2, and R3 refer to rings 1, 2, and 3 as designated in Fig. 1. [b] Numbers in parentheses are standard deviations from the average. [c] Values refer to the torsional angle of the chain of atoms. That these angles are very close to zero degrees implies that the four atoms are nearly planar.

groups. From the projection shown in Fig. 2 it is clear that the acetyl group is skewed relative to the rest of the structure. For example, the torsional angle O(6)-C(6)-Fe-C(5) is 39.2(6)° instead of the 45° angle needed for true mirror symmetry.

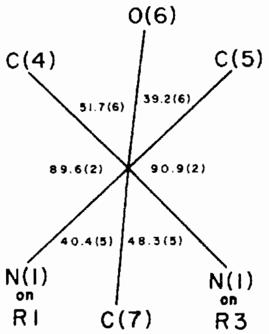

Figure 2. A projection down the C(6)-Fe-N(1) vector showing the orientation of the acetyl group relative to the rest of the molecule.

The important bond distances and angles are collected in Tables V and VI. The geometry about the iron atom has slight angular distortions from an octahedral arrangement of ligands. The main distortion is attributable to the non-orthogonal bite of the tridentate pyrazolylborate ligand. The N-Fe-N angles are 85.7(1)°, 86.0(1)°, and 88.7(1)°. These are somewhat larger than the average angles of 85.5(6)° and 81.8(3)° found for $(HBpz_3)_2Co$[13] and $(HBpz_3)(NNC_6H_5)(CO)_2Mo$.[2]

The Fe-N distances are 1.992(4), 1.999(3), and 2.082(4) Å. The average Fe-N distance, 2.024 Å, is significantly shorter than the average Co-N distance of 2.129(7) Å found in $(HBpz_3)_2Co$[13] and is *ca.* 0.02 Å shorter than the average Mo-N distances of 2.20(3), 2.21(3), and 2.22(1) Å reported for $[H_2B(3,5\text{-}Me_2pz)_2](C_7H_7)(CO)_2Mo$,[8] $(Bpz_4)(C_3H_5)(CO)_2Mo$,[7] and $(HBpz_3)(NNC_6H_5)(CO)_2Mo$,[2] respectively.

A comprehensive comparison of dimensions of dipyrazolylborate-metal six rings in all known, accurate structures will be found in a forthcoming paper in *Inorganic Chemistry* by L.J. Guggenberger, C.T. Prewitt, P. Meakin, S. Trofimenko, and J.P. Jesson (S. Trofimenko, private communication). We shall therefore omit further discussion of the pyrazolylborate-metal moiety, except for one feature whcih is peculiar to this compound.

The Fe-N distance *trans* to the acetyl group is 0.087 Å longer than the average of those *trans* to the carbonyl groups. This may be due to the fact that the acetyl group forms are essentially homopolar, strong single bond to the iron atom whereas the carbonyl groups form multiple bonds, the sigma components of which are probably weaker than the Fe-C-(acetyl) sigma bond. If we assume that the Fe-N bonds are mainly sigma donor bonds, it would appear that a sigma *trans* effect is operating here. A stronger sigma N-Fe bond can be formed *trans* to the relatively weak Fe-CO sigma bond than *trans* to the relatively strong Fe-C (acetyl) bond. Such an effect could be rationalized in terms of competition for the optimum mix of atomic orbitals in the two oppositely-directed sigma hybrid orbitals along a given octahedral bond axis.

The Fe-C distances for the carbonyl groups average 1.765(9) Å and, as expected, are substantially shorter than the acetyl Fe-C distance of 1.968(5) Å. The acetyl distance compares favorably with the Fe-C distance of 1.97(2) Å in the benzoyl structure $(C_5H_5)(COC_6H_5)(CO)[(C_6H_5)_3]Fe$.[14,15]

Both of the acyl Fe-C distances mentioned are significantly shorter than the alkyl Fe-C distance of 2.11 Å found in $(C_5H_5)(C_3H_5)(CO)[P(C_6H_5)_3]Fe$.[16]

A similar result has been obtained for Mo compounds where the Mo-acetyl and Mo-alkyl bond lengths are 2.264(14) Å and 2.383(10) Å in $(C_5H_5)(COCH_3)(CO)_5[P(C_6H_5)_3]Mo$[17] (the only other acetyl structure reported)[18] and $[(C_{10}H_8)(CH_3)(CO)Mo]_2$,[19] respectively. The shortening of the acyl bond is generally accounted for by invoking d_π-p_π metal-to-acyl back-donation.[15,17] This means that the Fe-C (acetyl) bond is not a pure sigma bond, although the sigma component is doubtless stronger and more dominant than in the Fe-CO bonds, in accord with the previously suggested explanation of the difference in Fe-N bond lengths.

The acetyl C-C bond length of 1.522(8) Å found in the present structure is in close agreement with the bonds of 1.550(20) Å and 1.505(13) Å found in the acetyl Mo compound[17] and in acetamide, H_2NCOCH_3.[20] The C-O bond length is 1.193 (6) Å and compares with reported acyl C-O bond distances: $(COC_6H_4Cl)(CO)_5Re$, 1.16(2) Å;[21] $(C_5H_5)(COCH_3)(CO)_2[P(C_6H_5)_3]Mo$, 1.21(2) Å;[17] $(C_5H_5)(COC_6H_5)(CO)[P(C_6H_5)_3]Fe$, 1.22(3) Å;[14] $(C_5H_5)(COC_6H_5)(CO)_2Mn^-$, 1.28(3) Å.[22] The bond angles associated with the acetyl ligand in the present work are Fe-C-O of 124.3(4)°, Fe-C-C of 119.0(4)°, and C-C-O of 116.7(5)°. These are reasonably close to the corresponding values of 120.9(10)°, 121.2(9)°, and 117.7(12)° found in the acetyl Mo complex[18] and also the average values of 123°, 121°, and 115° in two benzoyl structures.[15,22] However they differ markedly from the corresponding bond angles of 115°, 136°, and 109° in $(COC_6H_4Cl)(CO)_5Re$.[21]

As illustrated in Fig. 3, the bond angles associated with the H atoms in the pyrazolborate ligands show a displacement of the H atoms toward the B and Fe atoms. For H(1) and H(3) the average N-C-H

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(13) M.R. Churchill, K. Gold, and C.E. Maw, Jr., *Inorg. Chem.*, *9*, 1597 (1970).

(14) Yu.A. Chapovskii, V.A. Semion, V.G. Andrianov, and Yu.T. Struchkov, *Zh. Struckt. Khim.*, *9*, 1100 (1968); or *J. Struct. Chem.*, *9*, 990 (1968).

(15) V.A. Semion and Yu.T. Struchkov, *Zh. Struckt. Khim.*, *10*, 664 (1969); or *J. Struct. Chem.*, *10*, 563 (1969).

(16) V.A. Semion and Yu.T. Struchkov, *Zh. Struckt. Khim.*, *10*, 88 (1969); or *J. Struct. Chem.*, *10*, 80 (1969).

(17) M.R. Churchill and J.P. Fennessey, *Inorg. Chem.*, *7*, 453 (1968).

(18) Structural work on $(COCH_3)(CO)_4[P(C_6H_5)_3]Mn$ has been performed, but no numerical results have been published: R.J. Fredericks and T.H. Doyne, VIIIth International Congress of Crystallography, Stony Brook, New York, 1969, *Collected Abstracts* s157; or *Acta Crystallogr.*, *22*, s157 (1969).

(19) P.H. Bird and M.R. Churchill, *Inorg. Chem.*, *4*, 1734 (1965).

(20) W.C. Hamilton, *Acta Crystallogr.*, *18*, 866 (1965).

(21) I.S. Astakhova, A.A. Johannsson, V.A. Semion, Yu.T. Struchkov, K.N. Anisimov, and N.E. Kolobova, *J. Chem. Soc.* (*D*), 488 (1969).

(22) E. Hadicke and W. Hoppe, *Acta Crystallogr.*, *Sect. B*, *27*, 760 (1971).

angle of 117(2)° differs significantly from the average C-C-H angle of 133(2)°.

The shortest intermolecular contact not involving hydrogen atoms is 3.259(7) Å between O(6) and C(1) on R1. The hydrogen atom attached to this carbon atom is 2.42(8) Å from the oxygen. Other short contacts are: 2.5(1) Å between H(1) on R1 and H(3) on R2, 2.62(8) Å between O(4) and H(3) on R3, 2.7(1) Å between H on B and H(1) on R3, 2.7(1) Å between H(7,3) on the methyl group and H(1) on R2. All other distances are 2.8 Å or greater. Additional bond distances and bond angles calculated for the structure reported here are given in Table IV and V.

Solution Studies. Both ir and pmr spectra vary in appearance with the age of the solution and the history of the solid used to prepare the solutions. Infrared spectra were recorded on cyclohexane solutions; only with a saturated hydrocarbon solvent could the sharp, narrow bands necessary to allow resolution of the closely spaced groups of bands be obtained. However, for pmr spectra the necessity for higher concentrations and the avoidance of solvent overlap required the use of deuterochloroform and CS_2.

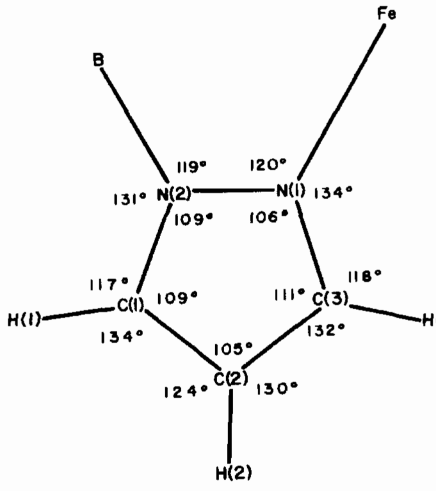

Figure 3. Average angles found in the pyrazolylborate ligand. The standard deviation on the average N-C-H and C-C-H angles is 2°, while an individual angle has an estimated standard deviation of 4° in R1 and R2 and 5° in R3.

When the ir spectrum of a cyclohexane solution of the acetyl compound is recorded immediately after making the solution from the freshly prepared crystalline compound, there are four bands in the terminal carbonyl stretching region at 2047, 2032, 1987 and 1973 cm^{-1} (all ± $1 cm^{-1}$) (see Fig. 4a) and two weaker bands in the region where the acetyl carbonyl stretch would be expected at 1683 and 1648 cm^{-1}.

When a solution of the type just described is allowed to stand, two additional bands appear, and gradually become more intense, in the terminal carbonyl stretching region, at 2028 and 1968 cm^{-1} (each ± 1 cm^{-1}). After 12-24 hours these bands cease growing relative to the original four bands. These two bands are due to the methyl compound, $(HBpz_3)(CH_3)(CO)_2Fe$, as will be shown below, and an assay by nmr (as described below) shows that the ratio of concentrations of the acetyl compound to the methyl compound is about 10: 1 when this steady state ir spectrum is reached. The steady-state ir spectrum is shown in Fig. 4b.

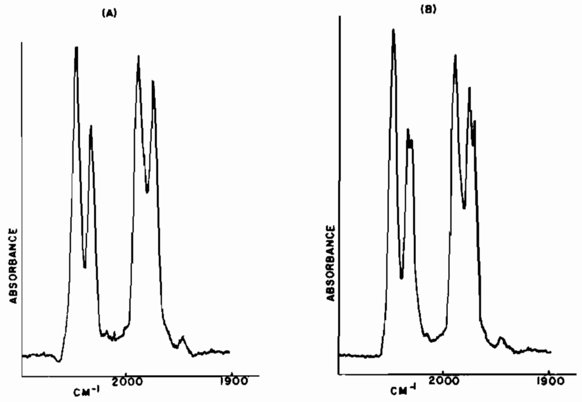

Figure 4 (a) A portion of the infrared spectrum of freshly prepared $(HBpz_3)(COCH_3)(CO)_2Fe$. (b) A portion of the « steady state » infrared spectrum of a solution of $(HBpz_3)(COCH_3)(CO)_2Fe$ which had been in the cell for 24 hours.

A cyclohexane solution preparated from a sublimed sample consisting of about 25% of the methyl compound (by nmr assay) has six terminal carbonyl streching bands right from the start as well as the two acetyl CO stretching bands. The relative intensity of the two bands due to the methyl compound decreases with time, over 6-12 hours, until the complete pattern of six terminal CO stretching bands becomes essentially identical to that obtained by starting with a sample of pure acetyl compound. In addition a new band grows in at ~1725 cm^{-1}, and the solution becomes more red in color. Evidently the methyl compound decomposes, giving rise to $(HBpz_3)_2Fe$ (which is responsible for the alteration and intensification of the color) and to some other product which we have not identiifed, that is responsible for the ir band at ~1725 cm^{-1}. The 1725 cm^{-1} band also eventually appears in solution initially made from the pure crystalline acetyl compound.

Over long periods of time, cyclohexane solutions decompose completely. Evidently, the sequence of events is:

$$\text{acetyl compound} \xrightarrow{k_1} \text{methyl compound} \xrightarrow{k_2} (HBpz_3)_2Fe + \text{other products}$$

The ratio of k_1 to k_2 at the temperature and other experimental conditions used leads to the persistence of an acetyl/methyl ratio of ~10: 1. It is also possible that the methyl compound may react, either with itself, or with CO still present in solution from earlier decomposition of the acetyl compound, to regenerate some of the acetyl compound.

Samples containing both the acetyl and the methyl compound give nmr spectra which show resonances due to both the methyl protons and the acetyl protons, which appear at τ7.68 and τ9.75, respectively in

$CDCl_3$. The pattern of resonances due to the ring protons of the pyrazole rings differs little from one compound to the other. The 3 and 5 protons appear as a multiplet of intensity 6 at τ2.28 and the 4 protons as slightly overlapping triplets of intensities 2 and 1 centered at τ3.75. In all nmr spectra the total intensity of the methyl and/or acetyl protons relative to the pyrazole ring protons was in the expected ratio of 3:9. The nmr spectra can be used to assay the acetyl/methyl ratio of the solute in a cyclohexane solution by rapidly evaporating the cyclohexane solution in vacuum at room temperature, , redissolving the solid residue in chloroform and immediately recording the nmr spectrum. This nmr assay was alluded to earlier.

Nmr spectra of chloroform solutions, run immediately, always give results which are consistent with the ir spectra run immediately on cyclohexane solutions with respect to the presence of the methyl compound and its relative concentration. In $CDCl_3$, however, the methyl compound is relatively shortlived and a solution prepared from a mixture relatively rich in the methyl compound has no trace of a methyl resonance after 12 hours, while the acetyl resonance remains. Chloroform solutions prepared from the pure acetyl compound never exhibit a resonance due to the CH_3 group of the methyl compound, presumably because the methyl compound decomposes as quickly as it is formed and thus cannot accumulate.

Even the solid, crystalline acetyl compound decomposes, albeit slowly. A week-old sample dissolved in cyclohexane had weak but very definite shoulders present in the ir spectrum at the frequencies characteristic of the methyl compound. These bands intensified over a period of about 12 hours until the steady state spectrum mentioned above was reached. As mentioned in the experimental section, crystal decomposition was also noticed during collection of the x-ray data.

Discussion

From the x-ray crystallographic results in particular, but also from other evidence, such as the molecular weights measured in solution and the ir and nmr spectra, the most important conclusion from this study emerges unequivocally. The bright yellow, crystalline solid obtained directly (without sublimation) from the preparative reaction is the acetyl compound, $(HBpz_3)(COCH_3)(CO)_2Fe$.

Freshly prepared solutions of this compound exhibit only a single peak in the nmr spectrum, aside from the resonances attributable to the pyrazole ring protons. This peak, at τ7.68 in $CDCl_3$ has an intensity 1/3 that of the total intensity of the resonances due to the nine pyrazolyl ring protons. Further the infrared spectra of freshly prepared solutions of the compound exhibit only four absorption bands in the region of terminal CO stretching and two bands in the region of acetyl CO stretching.

The spectroscopic results find a natural explanation in terms of isomers related by internal rotations of the acetyl group about the Fe-C bond. As shown in Fig. 5, there are four configurations which seem likely to correspond to minima in the potential energy as a function of rotational angle. Of these, A is that found in the crystal, while C and D are equivalent enantiomorphs. The infrared spectra indicate that only two nonequivalent rotomers are present in solution, in nearly but not exactly equal amounts. The nmr spectrum shows that these interconvert at a rate which is rapid on the nmr time scale.

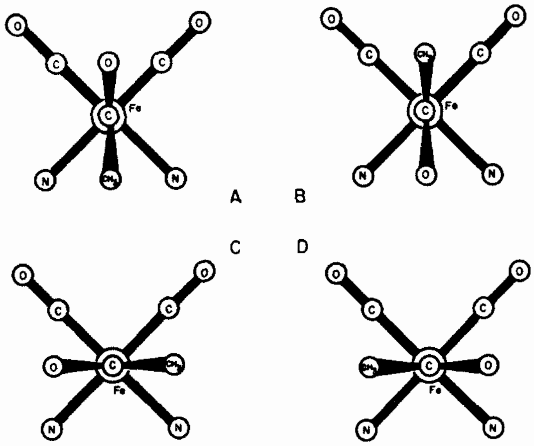

Figure 5. A diagrammatic representation of the four rotomers which involve a staggered relationship of the CH_3CO group to the remaining ligands.

The presence, in detectible quantities, of only two of the three distinguishable rotomers is not unusual for a molecule of this type. In the somewhat similar molecules , $(h^6\text{-arene})[C(OCH_3)(C_6H_5)](CO)_2Cr$,[23] $(h^5\text{-}C_5H_5)(CH_3SiCl_2)(CO)_2Fe$[24] and $(h^5\text{-}C_5H_5)(OCCH_3)(R_2NPF_2)(CO)Fe$[25] only two of the three different rotomers have been observed.

By inspection of a scale model of the molecular structure, as obtained from the crystal, it seems likely that the two rotomers present in solution are A and B. Using a model which is rigid except for rotational freedom about the Fe-C(O)CH_3 and FeC(O)-CH_3 bonds there are very close approaches (~2.4 Å) of the methyl group carbon atom to ring hydrogen atoms at the 3-positions of the two pyrazolyl groups which are *cis* to the acetyl group. Interconversion of rotomers A and B requires traversal of rotomers C and D; the rotational configurations with maximal energy may be judged from the model to be close to rotomers C and D. Without attempting to offer quantitative justification, we assert that it seems reasonable to believe: (1) that the barrier to rotational interconversion of A and B can be low enough ($\leqslant$10 kcal mol^{-1}) to allow rapid interconversion of the nmr time scale, and (2) that the free energy difference between A and B on the one hand and C and D on the other is great enough ($\geqslant$3 kcal mol^{-1}) to keep the concentra-

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(23) H.-J. Beck, E.O. Fischer, and C.G. Kreiter, *J. Organometal. Chem.*, *26*, C41 (1970).

(24) W. Jetz and W.A.G. Graham, *J. Amer. Chem. Soc.*, *89*, 2773 (1967).

(25) R.B. King, W.C. Zipperer, and M. Ishaq, *Inorg. Chem.*, *11*, 1361 (1972).

tions of C and D below the limits of detectibility (~1%).

The acetyl compound is thermally unstable, and this appears to be the reason for earlier confusion[4] as to its identity and behavior. Bruce, *et al.* isolated their product by sublimation. We find that the process of vacuum sublimation always causes some degree of decarbonylation. It therefore gives a mixture of the acetyl compound and the methyl compound on the cold probe. The exact extent of decomposition depends on pot temperature, length of beating time and probably other experimental conditions. Typically, about a 3:1 mixture of the acetyl and methyl compounds is obtained.

Partial degradation of the acetyl compound occurs also when solutions, or even the solid, are allowed to stand. A new pair of bands, at 2028 and 1973 cm^{-1} in cyclohexane, grows into the infrared spectrum, and a new peak, at τ9.75, grows into the proton nmr spectrum. The two new ir bands, lying only 4-5 cm^{-1} from the closest bands in the spectrum of the acetyl compound are not easily noticeable in spectra recorded under normal instrument operating conditions, but can readily be detected, either as shoulders, or separate peaks when the spectrum is recorded on an expanded scale.

The methyl compound is, of course, expected to have only two ir peaks since, aside from rotation about the Fe-CH_3 bond, the methyl compound is an essentially rigid molecule which has no conformational isomers. It is reasonable that the frequencies for the methyl compound should be lower than those for either rotomer of the acetyl compound because the methyl group is less electron withdrawing than the acetyl group. In the methyl compound, therefore there is more Fe→CO $d\pi \rightarrow \pi^*(CO)$ bonding which lowers the CO bond order.

Acknowledgement. We are very grateful to The Robert A. Welch Foundation for generous financial support of this work under Grant No. A-494.