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**Supplementary Material Available:** Listings of final positional and thermal parameters for the hydrogen atoms, least-squares planes, selected interplanar angles and atomic deviations, selected torsion angles, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

## Pyrazolyl-Bridged Iridium Dimers.<sup>1</sup> 4. Crystal and Molecular Structures of Bis(cycloocta-1,5-diene)bis( $\mu$ -pyrazolyl)diridium(I), Its Dirhodium(I) Isomorph, and Two Bis(cycloocta-1,5-diene)diridium(I) Analogues Incorporating 3,5-Disubstituted $\mu$ -Pyrazolyl Ligands

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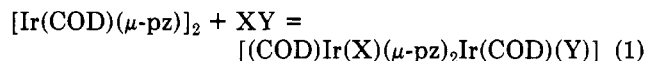
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The crystal and molecular structures of the homobimetallic complexes  $[M(\text{COD})(\mu\text{-pz})]_2$  (1, M = Ir, 2, M = Rh; COD = cycloocta-1,5-diene, pzH = pyrazole),  $[\text{Ir}(\text{COD})(\mu\text{-fpz})]_2$  (3, fpzH = 3,5-bis(trifluoromethyl)pyrazole), and  $[\text{Ir}(\text{COD})(\mu\text{-3-CH}_3\text{,5-CF}_3\text{C}_3\text{N}_2\text{H})]_2$  (4, derived from 3-methyl-5-(trifluoromethyl)pyrazole) have been determined by single-crystal X-ray diffraction. Compounds 1 and 2 are isomorphous, crystallizing in the space group *Cmcm* with  $a = 12.750$  (4) Å,  $b = 12.037$  (4) Å, and  $c = 13.432$  (4) Å and  $a = 12.745$  (4) Å,  $b = 12.019$  (4) Å, and  $c = 13.405$  (4) Å, respectively: the two molecules are virtually identical with Ir-Ir = 3.216 (1) Å in 1 and Rh-Rh = 3.267 (2) Å in 2, indicating that observed differences in reactivity originate from electronic effects. Compound 3, space group *P1* with  $a = 11.604$  (5) Å,  $b = 11.968$  (5) Å,  $c = 11.131$  (4) Å,  $\alpha = 95.10$  (4)°,  $\beta = 97.52$  (4)°, and  $\gamma = 110.32$  (3)°, is sterically crowded by the substituent  $\text{CF}_3$  groups in the  $\mu\text{-fpz}$  unit in a way which accords with the remarkably inert character of this complex compared with 1 and which may also be responsible for the significant contraction in Ir-Ir, to 3.073 (1) Å. The structure of compound 4 is disordered in terms of  $\text{CH}_3\text{,CF}_3$  site occupancy, but in this molecule also Ir-Ir is short at 3.066 (2) Å.

We recently described<sup>2</sup> the synthesis and some properties of the diridium(I) complex  $[\text{Ir}(\text{COD})(\mu\text{-pz})]_2$  (1, COD = cycloocta-1,5-diene, pzH = pyrazole). The rhodium analogue 2 of compound 1 was first reported in 1971 by Trofimenko.<sup>3</sup> We have demonstrated an unusual structure for 1, wherein despite being linked through two atoms in the heterocyclic bridge the  $d^8$  Ir centers are brought to close proximity (3.216 Å) and have uncovered an extensive chemistry a salient feature of which is<sup>2</sup> oxidative addition by a variety of substrates to give diridium(II) products without fragmentation of the dimeric unit (eq 1). We have



also established that parallel reactivity is not a property of compound 2 for which we find no evidence for formation

of isolable adducts with, for example, MeI or activated acetylenes. Complexes 1 and 2 do resemble each other, however, in that on treatment with CO, COD is displaced from either one to give an unstable tetracarbonyl dimer, which will react further with  $\text{PPh}_3$  affording the carbonyl phosphine analogues  $[\text{M}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})]_2$  (M = Rh or Ir). Each of the latter will undergo two-center oxidative addition, the  $\text{Ir}_2$  species being the more reactive, inter alia slowly forming a dihydrogen adduct and yielding cationic complexes with  $\text{HPF}_6$ . In this context we have already reported<sup>4</sup> an X-ray study of  $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})]_2$  and its

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 1-4

compd	1	2	3	4
mol wt	734.9	556.3	1006.9	899.0
cryst system	orthorhombic	orthorhombic	triclinic	monoclinic
space group	<i>Cmcm</i>	<i>Cmcm</i>	<i>P1</i>	<i>C2/c</i>
cell dimens				
<i>a</i> , Å	12.750 (4)	12.745 (4)	11.604 (5)	21.696 (5)
<i>b</i> , Å	12.037 (4)	12.019 (4)	11.968 (5)	13.619 (2)
<i>c</i> , Å	13.432 (4)	13.405 (4)	11.131 (4)	19.869 (5)
$\alpha$ , Å			95.10 (4)	
$\beta$ , Å			97.52 (4)	114.40 (4)
$\gamma$ , Å			110.32 (3)	
cell vol, Å <sup>3</sup>	2061	2053	1422	5347
molecules/unit cell	4	4	2	8
$\rho$ (calcd), g cm <sup>-3</sup>	2.37	1.80	2.35	2.23
$\mu$ (calcd), cm <sup>-1</sup>	124.5	15.8	100.3	106.2
radiatn	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
max cryst dimens, mm	0.05 $\times$ 0.05 $\times$ 0.10	0.05 $\times$ 0.05 $\times$ 0.14	0.10 $\times$ 0.42 $\times$ 0.45	0.08 $\times$ 0.19 $\times$ 0.82
scan width, deg	0.80 + 0.20 tan $\theta$	0.80 + 0.20 tan $\theta$	1.24	1.00
decay of stds	$\pm$ 2%	$\pm$ 2%	$\pm$ 2%	-21%
2 $\theta$ range	4-44	4-44	4-45	4-40
obsd reflectns	473	498	3389	1435
no. of parameters varied	67	67	397	187
<i>R</i>	0.022	0.034	0.090	0.091
<i>R</i> <sub>w</sub>	0.026	0.045	0.092	0.094

dichlorine addition product [Ir(CO)(PPh<sub>3</sub>)(Cl)( $\mu$ -4-Cl-pz)]<sub>2</sub>; the crystal structure of a rhodium(I) analogue, [Rh(CO)(P(O)Ph<sub>3</sub>)( $\mu$ -pz)]<sub>2</sub> has also been determined by Tiripicchio.<sup>5</sup>

Continuing our investigation of the chemistry of the iridium dimer 1, we have prepared an extensive family of related complexes differing from one another only in the pattern of substitution within the heterocyclic bridging ligand. Such products are typified by [Ir(COD)( $\mu$ -fpz)]<sub>2</sub> (3, fpzH = 3,5-bis(trifluoromethyl)pyrazole) and [Ir(COD)( $\mu$ -3-CH<sub>3</sub>,5-CF<sub>3</sub>C<sub>3</sub>N<sub>2</sub>H)]<sub>2</sub> (4), the latter derived from 3-methyl-5-(trifluoromethyl)pyrazole.<sup>6</sup> This led us to discover that by contrast with compound 1, 3 is conspicuously inert;<sup>7</sup> thus there was no sign of any reaction after refluxing (THF) with MeI or dmad (dimethyl acetylenedicarboxylate) for periods as long as 72 h. A plausible explanation for this remarkable lowering in reactivity emerges from the molecular geometry adopted by compound 3 in the solid state, established crystallographically: the CF<sub>3</sub> substituents at the 3,5 bridge positions are oriented in a way which severely curtails access to the axial site at Ir, introducing a very pronounced steric blocking effect. Further support for this interpretation is provided<sup>7</sup> by the sluggish reactivity toward oxidizing substrates of another dimer, [Ir(COD)( $\mu$ -dpz)]<sub>2</sub> (dpz = 3,5-dimethylpyrazole), when exposed to conditions under which adduct formation by 1 is very rapid; and by introduction of I in an equatorial position at Rh with elimination of terminal CO groups on reaction of [Rh(CO)(PPh<sub>3</sub>)( $\mu$ -dpz)]<sub>2</sub> with 1,2-C<sub>2</sub>H<sub>4</sub>I<sub>2</sub>, to give a rhodium product having vacant axial sites.<sup>8</sup> A further intriguing possibility is that the steric influence of bridge substitution may also be responsible for the marked reduction (0.143 Å) in Ir<sub>2</sub> separation between 1 and 3 through compression along the Ir<sub>2</sub> axis, a change which we believe<sup>2</sup> reflects a difference in degree of Ir-Ir bond character.

This paper reports in full the structure determination by X-ray diffraction of compounds 1-4. In summary, the analogues [M(COD)( $\mu$ -pz)]<sub>2</sub> (1, M = Ir; 2, M = Rh) are

isomorphous and have been shown to possess geometries that are almost superimposable, so that the observed differences in chemistry between the two may be attributed to electronic effects; by contrast the qualitatively similar change in reactivity between 1 and 3 appears to originate predominantly from steric influences. The fourth structure, that of 4, is complicated by disorder in terms of CH<sub>3</sub>/CF<sub>3</sub> site occupancy but is significant in that the Ir<sub>2</sub> separation (3.066 Å) is yet shorter than that identified in 3.

### Experimental Section

All synthetic work was conducted at the University of Victoria;<sup>2,4,7</sup> suitable crystals of compounds 1 through 4 were provided by Dr. A. W. Coleman and Mr. D. O. K. Fjeldsted. Crystallographic characterization of complexes 1 and 2 was accomplished at the University of Alabama, using an Enraf-Nonius CAD-4 unit; for 3 and 4 the data were collected on a Picker four-circle diffractometer automated with a PDP-11/10 computer at the University of Victoria.

**Data Collection and Structure Refinement.** **A. Compounds 1 and 2.** Crystal data for 1 (bright red plates) and 2 (yellow plates) are listed in Table I. 1 and 2 are isostructural, crystallizing in the space group *Cmcm* with the molecules lying around an "mm" crystallographic position: one mirror plane contains the two metals and the other contains the central carbon atoms of the pyrazolyl bridges. Patterson map inspection yielded the metal atom coordinates, and all non-hydrogen atom positions were revealed on subsequent difference Fourier maps. Following full-matrix least-squares refinement of all non-hydrogen atoms, pyrazolyl hydrogen atoms were located for both compounds and with these fixed upon the appropriate carbon atoms, final least-squares refinements led to *R* values of  $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$  of 0.022 and 0.034 and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}$  of 0.026 and 0.045 for 1 and 2, respectively. Patterson syntheses and full-matrix least-squares refinements were conducted by using the SHELX program package.<sup>9</sup> Neutral atom scattering factors for C, N, Rh, and Ir were taken from the compilations of Cromer and Mann,<sup>10</sup> whereas those for H were taken from ref 11. Corrections for the real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Libermann<sup>12</sup> and were applied to all atoms. All reflections were

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Table II. Final Fractional Atomic Coordinates for 1

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ir	0.62612 (6)	0.90449 (5)	0.2500
N	0.5536 (6)	0.8079 (7)	0.3585 (6)
C(1)	0.585 (1)	0.747 (1)	0.4363 (8)
C(2)	0.5000	0.706 (2)	0.487 (1)
C(3)	0.656 (1)	1.033 (1)	0.1448 (8)
C(4)	0.7415 (9)	0.959 (1)	0.144 (1)
C(5)	0.659 (1)	1.151 (1)	0.194 (1)
C(6)	0.8451 (9)	0.983 (2)	0.192 (1)

Table III. Final Fractional Atomic Coordinates for 2

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Rh	0.6282 (1)	0.9068 (1)	0.2500
N	0.5521 (6)	0.8130 (6)	0.3579 (6)
C(1)	0.5851 (9)	0.7522 (9)	0.4344 (8)
C(2)	0.5000	0.709 (2)	0.486 (1)
C(3)	0.7430 (9)	0.962 (1)	0.1445 (9)
C(4)	0.6585 (9)	1.0354 (9)	0.1442 (8)
C(5)	0.8477 (8)	0.983 (1)	0.193 (1)
C(6)	0.660 (1)	0.1505 (9)	0.1947 (9)

Table IV. Fractional Atomic Coordinates and Temperature Parameters for 3<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> , Å <sup>2</sup>
Ir(1)	67807 (7)	36166 (6)	76100 (7)	572 (4)
Ir(2)	76152 (7)	14538 (7)	72678 (7)	558 (4)
N(1)	7682 (14)	3254 (14)	9132 (15)	60 (7)
N(2)	8148 (12)	2400 (12)	9061 (14)	51 (6)
N(3)	5412 (13)	1978 (15)	7746 (14)	60 (7)
N(4)	5796 (14)	1035 (12)	7662 (15)	59 (6)
F(1)	7455 (23)	4535 (18)	12099 (15)	150 (13)
F(2)	6427 (19)	4575 (17)	10408 (17)	137 (10)
F(3)	8305 (21)	5737 (13)	10972 (18)	135 (10)
F(4)	8701 (14)	347 (12)	9775 (15)	96 (7)
F(5)	10480 (12)	1794 (14)	10166 (14)	97 (7)
F(6)	9399 (17)	1289 (17)	11586 (14)	123 (10)
F(7)	4113 (17)	3357 (16)	8779 (19)	130 (10)
F(8)	2611 (17)	1751 (18)	8892 (22)	149 (12)
F(9)	2860 (16)	2403 (17)	7214 (20)	130 (10)
F(10)	6247 (13)	-985 (12)	8538 (17)	111 (8)
F(11)	4411 (16)	-1640 (14)	8927 (17)	124 (9)
F(12)	4718 (18)	-1854 (13)	7121 (16)	116 (8)
C(1)	792 (2)	369 (2)	1035 (3)	87 (12)
C(2)	858 (2)	312 (2)	1110 (2)	78 (10)
C(3)	865 (2)	226 (2)	1013 (2)	65 (8)
C(4)	931 (2)	142 (2)	1038 (2)	72 (10)
C(5)	751 (3)	464 (2)	1099 (2)	93 (13)
C(6)	425 (2)	152 (2)	809 (2)	68 (9)
C(7)	394 (2)	35 (2)	824 (2)	79 (11)
C(8)	493 (2)	8 (2)	803 (2)	70 (9)
C(9)	510 (2)	-111 (2)	815 (2)	71 (9)
C(10)	346 (2)	226 (3)	824 (3)	103 (15)
C(11)	557 (2)	426 (2)	649 (2)	80 (10)
C(12)	607 (2)	371 (2)	580 (3)	94 (12)
C(13)	704 (3)	428 (4)	509 (3)	129 (20)
C(14)	829 (4)	505 (3)	588 (3)	139 (21)
C(15)	835 (3)	485 (2)	720 (3)	97 (12)
C(16)	790 (2)	548 (2)	802 (2)	90 (11)
C(17)	715 (4)	621 (3)	753 (3)	130 (20)
C(18)	596 (3)	557 (2)	674 (3)	128 (17)
C(21)	935 (2)	114 (3)	721 (3)	107 (15)
C(22)	938 (2)	221 (2)	678 (3)	94 (12)
C(23)	923 (3)	228 (4)	537 (4)	135 (20)
C(24)	804 (3)	158 (3)	462 (3)	126 (16)
C(25)	706 (2)	101 (2)	535 (3)	92 (12)
C(26)	696 (2)	-4 (2)	590 (2)	86 (12)
C(27)	794 (6)	-60 (4)	582 (4)	187 (34)
C(28)	918 (4)	7 (5)	642 (3)	151 (27)

<sup>a</sup> Estimated standard deviations are given in parentheses. Coordinates × 10<sup>n</sup> where *n* = 5, 4, 4, and 3 for Ir, F, N, and C, respectively. Temperature parameters × 10<sup>n</sup> where *n* = 4 for Ir and *n* = 3 otherwise. *U*<sub>eq</sub> = the equivalent isotropic temperature parameter. *U*<sub>eq</sub> = <sup>1</sup>/<sub>3</sub> Σ<sub>*i*</sub> Σ<sub>*j*</sub> *U*<sub>*ij*</sub> *a*<sub>*i*</sub> \* *a*<sub>*j*</sub> \* (*a*<sub>*i*</sub> *a*<sub>*j*</sub>).

Table V. Fractional Atomic Coordinates and Temperature Parameters for 4<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> , Å <sup>2</sup>
Ir(1)	32660 (8)	35676 (14)	26989 (8)	522 (9)
Ir(2)	17417 (8)	35712 (15)	17219 (9)	554 (9)
N(1)	2986 (15)	4533 (22)	1865 (18)	54 (9)
N(2)	2276 (15)	4592 (20)	1427 (17)	53 (9)
C(1)	3264 (21)	5149 (30)	1492 (22)	56 (11)
C(2)	2763 (18)	5568 (27)	859 (20)	47 (10)
C(3)	2159 (22)	5192 (31)	804 (24)	63 (12)
C(4)	1445 (23)	5301 (33)	174 (26)	66 (13)
F(1)	1602 (26)	5577 (37)	-281 (30)	87 (15)
F(2)	1124 (32)	5897 (49)	382 (34)	119 (20)
F(3)	1157 (34)	4463 (52)	-15 (37)	131 (22)
C(5)	4053 (26)	5229 (41)	1804 (30)	90 (16)
F(1P)	4323 (23)	4372 (39)	1895 (25)	77 (13)
F(2P)	4309 (22)	5743 (34)	2308 (25)	62 (12)
F(3P)	4147 (26)	5642 (38)	1191 (29)	90 (15)
N(3)	2968 (17)	2581 (23)	1857 (19)	63 (9)
N(4)	2258 (14)	2575 (20)	1390 (16)	43 (8)
C(6)	3284 (20)	1925 (27)	1597 (21)	44 (10)
C(7)	2831 (21)	1614 (29)	920 (23)	60 (12)
C(8)	2174 (21)	2016 (30)	824 (23)	56 (11)
C(9)	1457 (23)	1796 (32)	162 (26)	66 (13)
F(4)	1169 (23)	2704 (33)	7 (25)	70 (13)
F(5)	1561 (21)	1489 (29)	-422 (23)	56 (11)
F(6)	1087 (20)	1288 (29)	330 (22)	51 (11)
C(10)	4012 (24)	1853 (36)	1801 (26)	69 (13)
F(4P)	4314 (26)	1252 (37)	2407 (28)	86 (15)
F(5P)	4328 (30)	2588 (46)	1978 (32)	104 (19)
F(6P)	4177 (33)	1267 (43)	1320 (35)	116 (19)
C(11)	3253 (21)	2634 (32)	3555 (25)	69 (13)
C(12)	3903 (23)	2538 (32)	3441 (25)	72 (13)
C(13)	4570 (29)	2961 (44)	4000 (30)	106 (18)
C(14)	4506 (27)	4170 (41)	4090 (28)	95 (16)
C(15)	3921 (26)	4596 (36)	3525 (29)	92 (16)
C(16)	3277 (18)	4561 (26)	3420 (21)	45 (11)
C(17)	3148 (30)	4259 (51)	4131 (33)	127 (20)
C(18)	3155 (24)	3141 (35)	4158 (26)	77 (13)
C(19)	1443 (24)	4559 (33)	2300 (27)	76 (14)
C(20)	1019 (22)	4565 (31)	1602 (26)	72 (13)
C(21)	278 (33)	4170 (53)	1230 (37)	139 (22)
C(22)	260 (29)	3043 (43)	1287 (31)	105 (17)
C(23)	969 (23)	2540 (32)	1605 (26)	75 (14)
C(24)	1440 (26)	2597 (35)	2341 (28)	83 (15)
C(25)	1365 (27)	2918 (43)	3009 (31)	105 (18)
C(26)	1229 (28)	3874 (42)	2874 (29)	106 (18)

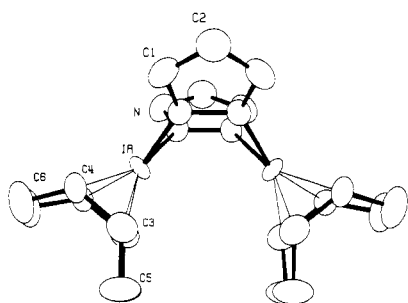
<sup>a</sup> Estimated standard deviations are given in parentheses. Coordinates × 10<sup>n</sup> where *n* = 5, 4, 4, and 4 for Ir, F, N, and C, respectively. Temperature parameters × 10<sup>n</sup> where *n* = 4, 3, 3, and 3 for Ir, F, N, and C, respectively. *U*<sub>eq</sub> = the equivalent isotropic temperature parameter. *U*<sub>eq</sub> = <sup>1</sup>/<sub>3</sub> Σ<sub>*i*</sub> Σ<sub>*j*</sub> *U*<sub>*ij*</sub> *a*<sub>*i*</sub> \* *a*<sub>*j*</sub> \* (*a*<sub>*i*</sub> *a*<sub>*j*</sub>). Primed values indicate that *U*<sub>iso</sub> is given. *T* = exp[-(8π<sup>2</sup> *U*<sub>iso</sub> (sin<sup>2</sup> θ) / λ<sup>2</sup>)].

corrected for Lorentz, polarization, and absorption (*μ* = 124.5 and 15.8 cm<sup>-1</sup>, respectively) effects, and no unaccountable electron density was evident on final difference Fourier maps. Final fractional atomic coordinates are listed in Tables II and III for the compounds 1, and 2, respectively.

**B. Compounds 3 and 4.** The crystal systems for 3 and 4 were found to be triclinic and monoclinic, respectively, from Weissenberg and precession photographs taken by using Cu radiation. Crystal data are included in Table I. The Ir atoms were located by a combination of direct methods and the Patterson function, the programs and constants used being identical with those detailed in section A. For compound 3 it was possible to refine all atoms by using anisotropic thermal parameters. By contrast for 4 only the Ir atoms could be refined in such a manner, and it was found that the Me and CF<sub>3</sub> groups in the substituted bridge were disordered; assigning an occupancy factor to each of 0.50 generated satisfactory temperature factors for the F atoms. Hydrogen atoms were not located in either structure; final values for *R* = 0.090 and 0.091 and for *R*<sub>w</sub> = 0.092 and 0.094 were obtained for 3 and 4, respectively. Final fractional coordinates are set out in Tables IV and V. All data were corrected for Lorentz, polarization, and absorption effects, and there were no unaccountable areas of

Table VI. Bond Distances (Å) and Angles (deg) for 1 and 2

	Ir	Rh
Distances		
(i) Metal Coordination		
M-M'	3.216 (1)	3.267 (2)
M-N	2.081 (8)	2.074 (8)
M-C(3)	2.13 (1)	2.14 (1)
M-C(4)	2.15 (1)	2.13 (1)
(ii) Pyrazolyl Ligands		
N-N'	1.37 (2)	1.33 (2)
N-C(1)	1.34 (1)	1.33 (1)
C(1)-C(2)	1.37 (2)	1.39 (1)
(iii) Cyclooctadiene Ligands		
C(3)-C(4)	1.41 (2)	1.39 (2)
C(3)-C(5)	1.56 (2)	1.51 (2)
C(4)-C(6)	1.50 (2)	1.54 (1)
C(5)-C(5')	1.50 (3)	1.54 (3)
C(6)-C(6')	1.55 (3)	1.48 (2)
Important Angles		
N-M-N	88.9 (5)	88.4 (4)
M-N-C(1)	136.2 (8)	133.6 (7)
C(1)-N-N	107 (1)	108 (1)
N-C(1)-C(2)	111 (1)	110 (1)
C(1)-C(2)-C(1)	104 (2)	103 (1)

Figure 1. ORTEP view of  $[\text{Ir}(\text{COD})(\mu\text{-pz})]_2$ .

electron density in the final difference Fourier maps.

### Results and Discussion

Important bond distances and angles for compounds 1 and 2 are presented in Table VI while those for compounds 3 and 4 are collected in Table VII. The molecular geometry for the diiridium complex (1) is represented as an ORTEP plot in Figure 1; a similar figure for the dirhodium isomorph 2, which is almost indistinguishable in appearance from Figure 1, has been filed with the supplementary material. The latter also includes a labeled molecular plot of the structure of compound 4 that, in view of the disorder explained above, omits F atoms but otherwise very closely

Table VII. Important Bond Distances (Å) and Angles (deg) for 3 and 4

	3	4
Distances		
Ir(1)-Ir(2)	3.073 (1)	3.066 (2)
N(1)-Ir(1)	2.03 (2)	2.00 (3)
N(2)-Ir(2)	2.11 (2)	2.04 (3)
N(3)-Ir(1)	2.08 (2)	2.03 (3)
N(4)-Ir(2)	2.11 (2)	2.03 (3)
C(11)-Ir(1)	2.15 (2)	2.12 (4)
C(12)-Ir(1)	2.10 (3)	2.09 (4)
C(15)-Ir(1)	2.05 (2)	2.18 (5)
C(16)-Ir(1)	2.13 (2)	1.97 (4)
C(21)-Ir(2)	2.17 (2)	2.04 (4)
C(22)-Ir(2)	2.10 (2)	2.01 (4)
C(25)-Ir(2)	2.11 (3)	2.14 (4)
C(26)-Ir(2)	2.09 (2)	2.09 (4)
Ir-N(av)	2.08	2.03
Ir-C(av)	2.11	2.08
3,5-Disubstituted Pyrazolyl Ligands		
N-N(av)	1.33	1.43
C-N(av)	1.35	1.37
C-C(ring)(av)	1.40	1.40
C-C(av)	1.51	1.55
C-F(av)	1.31	1.29
Cyclooctadiene Ligands		
C-C(av)	1.48	1.53
C=C(av)	1.37	1.39
Angles		
N(1)-Ir(1)-N(3)	82.5 (6)	82 (1)
N(2)-Ir(2)-N(4)	83.5 (5)	85 (1)
N(2)-N(1)-Ir(1)	121 (1)	115 (2)
N(4)-N(3)-Ir(1)	114 (1)	115 (2)
N(1)-N(2)-Ir(2)	109 (1)	113 (2)
N(3)-N(4)-Ir(2)	114 (1)	112 (2)
Ir(1)-N(1)-C(1)	134 (1)	141 (3)
Ir(1)-N(3)-C(6)	141 (1)	135 (3)
Ir(2)-N(2)-C(3)	137 (1)	136 (3)
Ir(2)-N(4)-C(8)	137 (1)	140 (3)

resembles half of the stereoview of the molecule of 3 depicted in Figure 2.

In each of the dimers 1-4 the individual metal centers are joined to one another by a pair of bridging, exo-bidentate pyrazolyl ligands defining a six-membered cyclic central framework that is common to all four structures. Departure of this unit from planarity is severe, and Figure 1 nicely illustrates the boatlike conformation that is adopted. In this arrangement the metal atoms approach each other to within 3.216 and 3.267 Å, respectively, for compounds 1 and 2, corresponding to inclination between the two independent square-planar coordination environments about M of 78.5° (Ir) or 80.7° (Rh). For these two molecules the overall structural similarity is overwhelming,

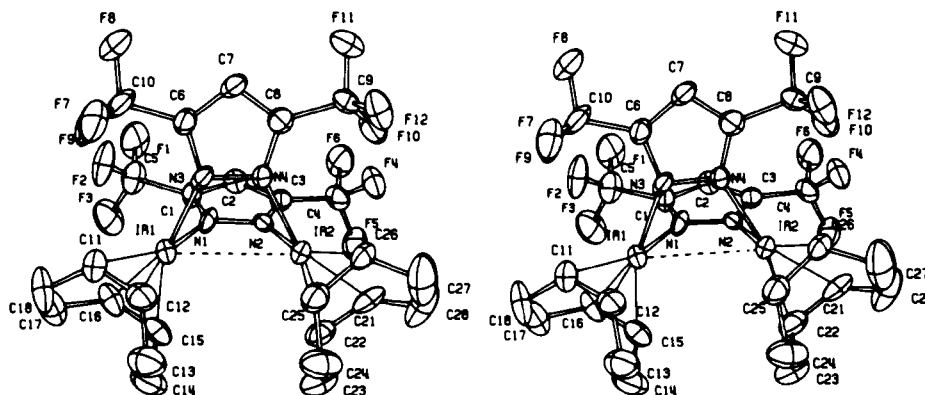
Figure 2. Stereoscopic view of  $[\text{Ir}(\text{COD})(\mu\text{-fpz})]_2$ .

Table VIII. Structurally Significant Nonbonding Distances (Å)

compd	M ··· M/ $\theta^a$	C ··· C <sup>b</sup>	C ··· C <sup>c</sup>	H ··· H <sup>d,f</sup>	H ··· H <sup>e,f</sup>
1	3.216 (1)/78.5	3.98	4.05	2.16	2.29
2	3.267 (2)/80.7	4.04	4.08	2.25	2.31
3	3.073 (1)/70.1	3.76	3.81	1.99	2.03
		3.80	3.85	1.98	2.11
4	3.066 (2)/69.7	3.66	3.61	1.84	1.72
		3.68	3.91	1.93	2.45

<sup>a</sup>  $\theta$  = angle between coordination planes about M (deg). <sup>b</sup> Nonbonding approach of COD olefinic C atoms. <sup>c</sup> Nonbonding approach of COD methylene C atoms. <sup>d</sup> Nonbonding approach of COD olefinic H atoms. <sup>e</sup> Nonbonding approach of COD methylene H atoms. <sup>f</sup> Hydrogen positions calculated assuming C-H = 1.07 Å.

and we therefore suggest that the lower reactivity of the Rh complex referred to in the Introduction may be explained by electronic differences of the same type as those that lead to the well-established divisions between the properties of Rh(I) and Ir(I) in mononuclear d<sup>8</sup> complexes. It is also clear that, as in<sup>4</sup> [Ir(CO)(PPh<sub>3</sub>)( $\mu$ -pz)]<sub>2</sub>, the short but formally nonbonding M<sub>2</sub> distances (1, M = Ir; 2, M = Rh) may reflect some degree of metal-metal interaction related to that confirmed by experiment to exist between adjacent Rh(I) centers in "face-to-face" dimers like the cation<sup>13</sup> Rh<sub>2</sub>[ $\mu$ -CN(CH<sub>2</sub>)<sub>3</sub>NC]<sub>4</sub><sup>2+</sup>. This possibility is currently being explored further by means of a detailed spectroscopic investigation, the results of which will be reported separately.

By contrast the disparity in terms of reactivity between the diiridium complex 3 and its prototypal analogue 1 seems to be accountable for on the basis of structural differences that can be identified directly from the X-ray data. In particular the steric crowding generated by the bridge trifluoromethyl substituents in the vicinity of the axial position at Ir in 3 is conspicuous in Figure 2; indeed this conveys an impression of nearly spherical space occupancy about the dimetal center by the organic framework of the ligands. Such a view is reinforced on closer consideration of the relative orientations of the terminal COD ligands and the pyrazolyl CF<sub>3</sub> groups. Thus calculation of the coordinates for the COD ethylenic hydrogen atoms<sup>14</sup> H(11), H(16), H(21), and H(26) places each of these latter between a pair of F atoms in a "lock-and-key" situation in which internuclear separations are well within the sum of the van der Waals radii for H and F (2.55 Å). The predictable effect of this arrangement will be to restrict access to the axial coordination position at Ir, hindering addition of a potentially reactive substrate by whatever mechanism and providing a rationale for the

relatively inert character of the complex.

There is also a marked contraction of the Ir<sub>2</sub> distance between 1 and 3, from 3.216 to 3.073 Å. It seems likely that here again the steric demand of the CF<sub>3</sub> substituents projecting from the pyrazolyl bridges is a major contributing factor, and accordingly a significantly closer approach of the terminal COD carbocycles is evident below (i.e., parallel to) the Ir<sub>2</sub> axis (Table VIII). Crowding arising in a similar way may be invoked to explain the almost linear I-Ir-Ir-I arrangement<sup>8</sup> in the related (oxidized) diiridium(II) complex [Ir(CO)P(OMe)<sub>3</sub>(I)( $\mu$ -3,5-dpz)]<sub>2</sub>; that this represents a substantial deviation from ideal geometry is obvious when the structure is compared with that<sup>4</sup> of [Ir(CO)(PPh<sub>3</sub>)(Cl)( $\mu$ -4-Clpz)]<sub>2</sub>. Further support for a steric (rather than electronic) effect as the origin for the compression along the Ir<sub>2</sub> vector is offered by the crystallographic data for complex 4: here the Me and CF<sub>3</sub> substituents would be predicted to exert quite different electronic influences, but in fact the Ir<sub>2</sub> separation of 3.066 Å closely resembles that in 3. Finally we note that the Ir<sub>2</sub> distances in the diiridium(I) complexes 3 and 4, though formally nonbonding, are in fact shorter than those in the oxidized MeI and I<sub>2</sub> adducts<sup>2,15</sup> of compound 1, each of which is dimeric, diamagnetic Ir(II) requiring the existence of an Ir-Ir single bond in terms of a conventional d<sup>7</sup>-d<sup>7</sup> formalism.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters for [Ir(COD)( $\mu$ -pz)]<sub>2</sub>, [Rh(COD)( $\mu$ -pz)]<sub>2</sub>, and [Ir(COD)( $\mu$ -fpz)]<sub>2</sub>, of bond distances and angles for [Ir(COD)( $\mu$ -fpz)]<sub>2</sub>, [Ir(COD)( $\mu$ -3-CH<sub>3</sub>,5-CF<sub>3</sub>C<sub>3</sub>N<sub>2</sub>H)]<sub>2</sub>, of least-squares planes for 1-4, and structure factor amplitudes for 1-4 and ORTEP drawings of [Rh(COD)( $\mu$ -pz)]<sub>2</sub> and [Ir(COD)( $\mu$ -3-CH<sub>3</sub>,5-CF<sub>3</sub>C<sub>3</sub>N<sub>2</sub>H)]<sub>2</sub> (42 pages). Ordering information is given on any current masthead page.

(13) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* 1981, 103, 1593. Dallinger, R. F.; Miskowski, V. M.; Gray, H. G.; Woodruff, W. H. *Ibid.* 1981, 103, 1595.

(14) Assuming C-H = 107 Å. A reviewer has remarked that while the steric effects described for complex 3 might be expected to restrict attack at Ir on the exo face, corresponding inhibition of possible endo entry is not so clear. We agree with this comment; however, close approach of the COD ring systems intrudes into the endo vicinity in the present structure (see Table VIII), a feature which is being investigated further in an X-ray study of another diiridium complex incorporating substituted pyrazolyl bridging ligands.

(15) Ir-Ir = 3.085 Å in [Ir(COD)(I)( $\mu$ -pz)]<sub>2</sub>; Atwood, J. L.; Coleman, A. W.; Stobart, S. R.; Zaworotko, M. J., to be submitted for publication.