

The positions of the remaining non-hydrogen atoms were obtained from subsequent Fourier and difference Fourier calculations.

Least-squares refinement¹⁹ of the 20 non-hydrogen atoms using 737 data with $I > 3\sigma(I)$ and allowing all the atoms to vary isotropically produced unweighted and weighted residuals of 0.072 and 0.067, respectively.²⁰ The positions of the hydrogen atoms were calculated by using a C-H distance of 0.95 Å and an isotropic thermal parameter of 5.0. Further full-matrix least-squares refinement using 866 reflections having $I > 2\sigma(I)$ and allowing all the heavy atoms except the cyclopentadienyl and phenyl carbon atoms to vary anisotropically converged with residuals $R = 0.074$ and $R_w = 0.052$.²¹ The final difference Fourier map shows no peaks with intensity greater than $0.29 \text{ e}/\text{Å}^3$.²²

(19) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

(20) $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and $\rho = 0.01$ is a correction factor.

(21) $R_{\text{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{\text{weighted}} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

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Registry No. 1 (isomer 1), 98689-87-3; 1 (isomer 2), 98757-40-5; 2, 98689-89-5; 3, 34742-22-8; 4, 93756-36-6; 5, 98689-88-4; allylamine, 107-11-9; diethylamine, 124-40-3; carbon, 7440-44-0; nitrogen, 7727-37-9.

Supplementary Material Available: Tables of anisotropic and isotropic thermal parameters, calculated hydrogen positions, complete bond distances and angles, least-squares planes coordinates and dihedral angles, and calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

(22) Scattering factors were taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press; Birmingham, England, 1974; Vol. IV, Table 2.2.

Pyrazolyl-Bridged Iridium Dimers. 8. Two-Center, Electrophilic Addition of Activated Acetylenes to Bis(cycloocta-1,5-diene)bis(μ -pyrazolyl)diiridium(I) Leading to a Diiridacyclobutene Configuration: Regular, Parallel Coordination of Methyl Propiolate

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The activated alkynes hexafluorobut-2-yne (HFB), dimethyl acetylenedicarboxylate (DMAD), and methyl propiolate (MPL) react under mild conditions with $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (1) to afford 1:1 adducts 2-4, respectively, for which ^1H and ^{13}C NMR measurements suggest "parallel" alkyne addition, generating a diiridacyclobutene configuration in which the two metal centers are formally d^7 Ir(II). By contrast the related diiridium(I) complex $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})_2]$ (5) forms a similar adduct (6) only with DMAD; with HFB alkyne polymerization occurs, attributed to PPh_3 dissociation from 5. Compounds 3 and 4 have been structurally characterized by using X-ray diffractometry, showing the geometry in each case to resemble that communicated earlier for 2 and substantiating the interpretation of the spectroscopic data. Crystal data for 3: space group $P2_1/c$, $a = 11.318$ (3) Å, $b = 11.543$ (3) Å, $c = 42.091$ (9) Å, $\beta = 98.07$ (3)°. Crystal data for 4: space group $P1$, $a = 10.983$ (4) Å, $b = 12.585$ (6) Å, $c = 9.862$ (4) Å, $\alpha = 92.96$ (4)°, $\beta = 110.29$ (3)°, $\gamma = 99.41$ (4)°. The adjacent Ir(II) centers in each molecule are spin paired via Ir-Ir bond formation, with single bond distances of 2.633 (2), 2.642 (2) Å (3, two independent molecules), and 2.637 (1) Å (4), to accommodate which terminal COD ligands are rotated to occupy axial positions at each Ir with alkyne coordination in equatorial sites. Coordination of the unsymmetrical MPL bridging unit is regular with Ir-C_{MPL} distances equal at 2.094 (mean) Å.

Introduction

Molecular orbital methods have recently been used by Hoffmann and co-workers² to develop a comparison in theoretical terms between parallel (A) and perpendicular (B) bridging orientations in binuclear transition-metal acetylene complexes, together with an analysis of possible pathways for interconversion between the two bonding modes. The parallel (dimetallacyclobutene) configuration

A has been encountered much less often^{2,3} than the alternative B: indeed the former is restricted almost exclusively to products arising from reactions of electron-deficient alkynes (typically $\text{R} = \text{CF}_3$ or CO_2Me), in which

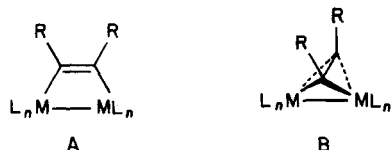
(1) Part 7: Bushnell, G. W.; Fjeldsted, D. O. K.; Stobart, S. R.; Zaworotko, M. J.; Knox, S. A. R.; Macpherson, K. A. *Organometallics* 1985, 4, 1107.

(2) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* 1982, 104, 3858. (b) Hoffman, D. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* 1982, 1471.

(3) Boag, N. M.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1980, 1281.

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the dimetal fragment behaves as a nucleophile and the geometry of the resulting adduct suggests a dianionic formalism for the coordinated acetylene.²



The behavior of HFB (hexafluorobut-2-yne, $\text{CF}_3\text{C}\equiv\text{CCF}_3$) or DMAD (dimethyl acetylenedicarboxylate, $\text{MeCO}_2\text{C}\equiv\text{CCO}_2\text{Me}$) toward bis(cycloocta-1,5-diene)bis-(μ -pyrazolyl)diiridium(I), $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (1, pzH = pyrazole), provides a further illustration of electrophilic alkyne addition involving two metal centers,⁴ affording the diiridacyclobutenes $[\text{Ir}_2(\text{COD})_2(\mu\text{-pz})_2(\mu\text{-C}_2\text{R}_2)]$ (2, $\text{R} = \text{CF}_3$; 3, $\text{R} = \text{CO}_2\text{Me}$). A preliminary description of the X-ray crystal structure of the HFB adduct 2 has been given previously.⁴ It was therefore of interest to see what if any perturbation to the parallel bonding mode A would result from incorporation of an unsymmetrically substituted alkyne: accordingly when we found that methyl propiolate, $\text{CH}\equiv\text{CCO}_2\text{Me}$ (MPL), reacted with complex 1 to form an adduct (4), a further crystallographic study was undertaken to establish the geometry of MPL coordination and to compare the latter with the result of HFB or DMAD addition across the Ir_2 axis. In this way the effect of introducing a third bridging fragment into the very stable^{5,6} dipyrazolyldiiridium framework has been examined, emphasizing that approach of the two Ir atoms to within bonding distance in diiridium(II) configurations derived from compound 1 can be accommodated only¹ by twisting of the terminal COD ligands to occupy axial sites at Ir.

The action of DMAD, MPL, and HFB on the dimer⁷ $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})_2]$ (5) has also been investigated. Adduct formation was observed only with DMAD: there was no evidence for addition of MPL, while polymerization of HFB was found to occur paralleling that⁸ induced by free triphenylphosphine.

Experimental Section

All synthetic work was carried out at the University of Victoria, using conventional inert-atmosphere techniques and standard methods for purifying and drying solvents. The diiridium(I) complexes $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (1) and $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})_2]$ (5) were prepared as described previously.^{1,5,7} DMAD (Aldrich) was distilled in vacuo before use; MPL (Aldrich) and HFB (PCR Research Chemical) were used as supplied. IR spectra were recorded on KBr pellets using a Perkin-Elmer 283 spectrophotometer. Hydrogen-1 and carbon-13 NMR spectra were obtained by using a Bruker WM250 FT instrument; Fluorine-19 data were recorded with a Perkin-Elmer R32 unit. Microanalytical data were supplied by Canadian Microanalytical Service, Vancouver.

Synthesis of Compounds. $\text{Ir}_2(\text{COD})_2(\mu\text{-pz})_2(\mu\text{-HFB})$ (2). Onto a frozen solution of $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (1, 0.34 g, 0.46 mmol) in THF (50 mL) was condensed HFB (3 g, excess) at -196°C . After being warmed to ambient temperature the initially red reaction mixture was stirred for 12 h under ca. 2-atm pressure of HFB affording a yellow solution. Evacuation to remove excess

acetylene and concentration to ca. one-third volume followed by addition of hexane and cooling to -25°C yielded the product 2 as pale yellow crystals (0.30 g, 0.33 mmol; 72%). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{F}_6\text{Ir}_2\text{N}_4$: C, 34.81; H, 3.37; N, 6.52. Found: C, 35.67; H, 3.52; N, 5.91. IR (cm^{-1}): 2965 m, br, 2850 m, 1570 m, 1383 m, 1301 m, 1220 s, 1200 s, 1120 s, 1090 s, br, 1056 s, 1042 s, 828 m, 732 s, 680 m, 632 m. NMR: ^1H (CD_2Cl_2 solution, δ vs. internal Me_4Si) 7.69 (2, d), 6.84 (2, d), 6.19 (1, t), 5.63 (1, t and 2, m), 5.04–2.15 (22, br, m), ^{13}C (CD_2Cl_2 solution, δ vs. Me_4Si) 138.9, 135.0 ($\mu\text{-pz C}^{3,5}$), 105.5, 104.2 ($\mu\text{-pz C}^4$), 87.6, 86.6, 79.4, 76.5 (COD CH), 35.5, 33.2, 29.9 and 27.8 (COD CH_2); ^{19}F (CD_2Cl_2 solution) 56.3 (s) ppm upfield vs. CFCl_3 .

$\text{Ir}_2(\text{COD})_2(\mu\text{-pz})_2(\mu\text{-DMAD})$ (3). To $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (0.10 g, 0.14 mmol) in THF (10 mL) was added DMAD (0.1 mL, excess). Stirring (12 h) at 20°C was accompanied by a slow change in color of the reaction mixture from red to yellow. Removal of solvent in vacuo left a viscous, brown oil to which was added THF (3 mL) and then Et_2O (5 mL) leading to slow deposition of yellow-brown crystals. Recrystallization from THF/hexane at -25°C afforded the product 3 as pale yellow, well-formed platelets (0.05 g, 0.06 mmol; 42%). Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{Ir}_2\text{N}_4\text{O}_4$: C, 38.34; H, 4.13; N, 6.38. Found: C, 38.55; H, 4.05; N, 6.31. IR (cm^{-1}): 2945 m, br, 2845 m, 1708 s, 1698 s, 1570 w, br, 1385 m, 1200 s, br, 1050 ms, 1011 m, 762 m. NMR: ^1H (CD_2Cl_2 solution, δ vs. internal Me_4Si) 7.57 (2, d), 6.85 (2, d), 6.13 (1, t), 5.65 (1, t), 5.35 (2, m), 4.76 (2, m), 4.23 (4, m), 3.65 (6, s), 2.51–2.05 (16, br, m); ^{13}C (CD_2Cl_2 solution, δ vs. Me_4Si) 172.0 (CO_{ester}), 138.4, 133.5 ($\mu\text{-pz C}^{3,5}$), 105.9 (C_{alkyne}), 104.5, 103.6 ($\mu\text{-pz C}^4$), 81.7, 80.4, 79.5, 75.6 (COD CH), 51.0 (OCH_3), 34.0, 32.9, 29.1, 27.2 (COD CH_2).

$\text{Ir}_2(\text{COD})_2(\mu\text{-pz})_2(\mu\text{-MPL})$ (4). To $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (0.15 g, 0.21 mmol) in THF (20 mL) was added MPL (0.1 mL, excess). The color of the reaction mixture slowly became paler, becoming orange during stirring at 20°C until after 24 h the volume was reduced to 5 mL and then hexane was added slowly to form an upper layer. Cooling to -25°C led to formation of orange-brown crystals (0.15 g, 0.18 mmol; 88%). Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{Ir}_2\text{N}_4\text{O}_2$: C, 36.63; H, 4.15; N, 6.84. Found: C, 37.36; H, 4.19; N, 6.60. IR (cm^{-1}): 2945 m, 2840 m, 1685 s, 1540 w, 1475 w, 1385 m, 1370 w, 1330 w, 1303 w, 1282 w, 1195 s, br, 1050 ms, 1027 m, 730 m. NMR: ^1H (CD_2Cl_2 solution, δ vs. internal Me_4Si) 8.76 (1, s), 7.62 (1, d), 7.49 (1, d), 6.92 (1, d), 6.77 (1, d), 6.10 (1, t), 5.71 (1, m), 5.65 (1, t), 4.85 (1, m), 4.52 (1, m), 4.46 (1, m), 4.21 (2, m), 4.00 (1, m), 3.77 (1, m), 3.66 (3, s), 2.60–1.60 (16, br, m); ^{13}C (CD_2Cl_2 solution, δ vs. Me_4Si) 139.7, 138.7, 134.1, 132.9 ($\mu\text{-pz C}^{3,5,5'}$), 115.3 ($\text{CH}_{\text{alkyne}}$), 104.3, 103.7 ($\mu\text{-pz C}^{4,4'}$), 101.0 ($\text{CCO}_2\text{Me}_{\text{alkyne}}$), 81.2, 81.0, 80.2, 79.5, 78.9, 75.2, 74.9 (COD CH), 51.2 (OCH_3), 36.5, 34.7, 33.7, 30.7, 30.6, 28.8, 28.4 (COD CH_2).

$\text{Ir}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-pz})_2(\mu\text{-DMAD})$ (6). To a suspension of $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})_2]$ (0.110 g, 0.10 mmol) in toluene (40 mL) and hexane (30 mL) was added excess (three drops) DMAD. After 10 min the initially orange-yellow color was completely discharged yielding a colorless solution. Removal of solvent followed by evacuation (4 h) left a pale yellow residue which was washed with hexane (3×10 mL). Recrystallization from toluene/hexane at -25°C afforded the product as pale cream microcrystals (0.10 g, 0.80 mmol; 80%). Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{F}_6\text{Ir}_2\text{N}_4\text{O}_2\text{P}_2$: C, 48.4; H, 3.41; N, 4.51. Found: C, 48.6; H, 3.65; N, 4.43. IR (cm^{-1}) 3050 w, 2945 w, 2042 w, sh, 1990 vs, 1690 s, 1538 w, 1478 mw, 1430 mw, 1430 m, 1380 mw, 1260 w, 1210 m, br, 1085 m, 1050 m, br, 800 w, 735 s, 686 s, 610 w, 570 w, 528 s, 512 s. NMR: ^1H (CD_2Cl_2 solution, δ vs. internal Me_4Si) 7.70–7.10 (32, br, m), 6.66 (1, d), 6.60 (1, d), 5.95 (1, t), 5.87 (1, dd), 3.12 (3, s), 3.08 (3, s).

X-ray Data Collection and Structure Refinement.⁹

Compound 3. A monoclinic crystal, space group $P2_1/c$, of the adduct 3 (transparent plates) suitable for X-ray diffraction was mounted and sealed in a thin-walled glass capillary. The crystal was oriented on a Nonius CAD4 diffractometer. The unit cell was refined by least squares from a list of centered reflections. The data collection was by conventional methods, and the experimental parameters are collected in Table I. The intensity data were corrected for Lorentz and polarization effects. No

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(7) (a) Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Atwood, J. L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 920. (b) Atwood, J. L.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1984**, *23*, 4050.

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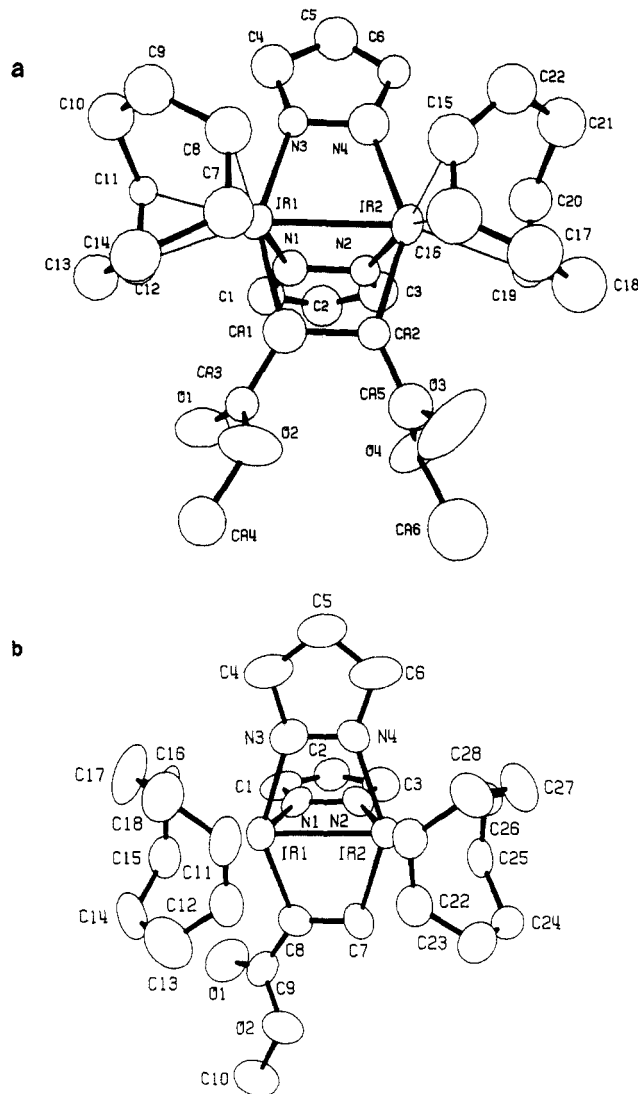
(9) The structure of compound 3 was determined at the University of Alabama using an Enraf-Nonius CAD4 diffractometer. The structure of compound 4 was determined at the University of Victoria using a Picker four-circle diffractometer automated with a PDP 11/10 computer.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 3 and 4

| | 3 | 4 |
|------------------------------|---|---|
| formula | C ₂₈ H ₃₆ Ir ₂ N ₄ O ₄ | C ₂₆ H ₃₄ Ir ₂ N ₄ O ₂ |
| mol wt | 877.0 | 819.0 |
| diffractometer | Nonius CAD-4 | Picker |
| cell dimensns | | |
| a, Å | 11.318 (3) | 10.983 (4) |
| b, Å | 11.543 (3) | 12.585 (6) |
| c, Å | 42.091 (9) | 9.682 (4) |
| α, deg | | 92.96 (4) |
| β, deg | | 110.29 (3) |
| γ, deg | 98.07 (3) | 99.41 (4) |
| cell vol, Å ³ | 5445 | 1230 (1) |
| molecules/unit cell | 8 | 2 |
| ρ(calcd), g cm ⁻³ | 2.14 | 2.21 |
| μ(calcd), cm ⁻¹ | 104.1 | 115.0 |
| radiatn | Mo Kα (monochrom) | Mo Kα (Zr filter) |
| max crystal dimensns, mm | 0.05 × 0.15 × 0.20 | 0.11 × 0.22 × 0.08 |
| scan technique | ω/2θ | θ/2θ |
| scan width | 0.80 + 0.20 tan θ | 1.00 |
| decay of std | ±2% | ±2% |
| 2θ range, deg | 4–44 | 0–45 |
| obsd reflectns | 4049 | 3222 |
| no. of parameters varied | 365 | 307 |
| GOF | 0.9 | |
| R | 0.070 | 0.066 |
| R _w | 0.080 | 0.058 |
| space group | P2 ₁ /c | P1̄ |

absorption correction was applied because the crystal was small and irregular in shape. The direct methods program MULTAN¹⁰ was used to determine the coordinates of iridium atoms, and remaining non-hydrogen atoms were found from difference maps phased upon the heavy atoms.¹¹ There were two distinct molecules in the asymmetric unit. Following full-matrix least-squares refinement with isotropic temperature factors for all atoms except the iridium and oxygen atoms, which were refined anisotropically, final values of $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2}$ were 0.070 and 0.080, respectively. Final fractional coordinates are listed in Table II. Neutral atom scattering factors were taken from the compilations of Cromer and Mann¹² and corrections for anomalous dispersion from ref 13. No unaccountable electron density further than 1 Å away from the iridium atoms was evident.

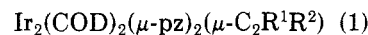
Compound 4. The triclinic crystal was photographed on Weissenberg and precession cameras to establish the space group, $P\bar{1}$, and cell. The unit cell was refined by least squares from 24 pairs of $\pm 2\theta$ measurements. The measured density (2.17 g cm⁻³, by flotation in CCl₄/CHBr₃) was consistent with the cell and formula. Crystal data are given in Table I. Intensities were measured by a stepped scan of 100 steps of 0.01° in 2θ counting for 0.5 s/step and background counts for 25 s at each end of the scan. Measurements were done for the hemisphere $h \geq 0$. Three standards 040, 500, and 002 preceded each batch of 50 reflections and were used in scaling. There was no noticeable decline in the intensities of the standards during the data collection period. Lorentz and polarization corrections were applied. Absorption corrections were done by numerical integration over crystal volume using an $8 \times 16 \times 8$ Gaussian grid, and the transmission range was 0.19–0.39. The structure was solved by using the direct methods part of the program SHELX-76.¹⁴ Atomic scattering factors were as described above, and refinement was carried out by using

**Figure 1.** Molecular geometry of (a) compound 3 and (b) compound 4.

standard Fourier and least-squares methods. The function minimized was $\sum w\Delta^2$ where the weights are given by $w = 1/(\sigma^2(F) + 0.001F^2)$, and $\Delta = ||F_o| - |F_c||$. Refinement converged at $R = 0.066$ with the maximum shift/esd being 0.06. All reflections were included. The final difference map had a maximum of $2.9 \text{ e } \text{Å}^{-3}$ and a minimum of $-2.3 \text{ e } \text{Å}^{-3}$. All peaks above $1 \text{ e } \text{Å}^{-3}$ were close to the Ir atoms, indicating no omission of atoms. The fractional coordinates are given in Table III.

Results and Discussion

Slow discharge of the characteristic purple-red color of $[\text{Ir}(\text{COD})(\mu\text{-pz})_2]$ (1) occurs in the presence of excess HFB, DMAD, or MPL to afford pale yellow, crystalline adducts (2, 3, or 4, respectively), each of which may be isolated in close to quantitative yield. Equimolar uptake of activated acetylene by the diiridium(I) complex (i.e., eq 1) is confirmed by analytical data. IR spectra of the products

$$[\text{Ir}(\text{COD})(\mu\text{-pz})_2]_2 + \text{C}_2\text{R}^1\text{R}^2 =$$


include absorptions attributable to $\nu(\text{C}-\text{F})$ and $\nu(\text{C}=\text{O})$ as appropriate but are otherwise rather uninformative. Some structural insight is provided however by ¹H NMR spectra in the δ 5.5–7.8 region, in which resonances due to protons attached to the bridging pz ligands are well resolved at 250 MHz. For each of the adducts with sym-

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(11) Utilizing the SHELX program package written by G. M. Sheldrick. Other programs used on a UNIVAC 1100 computer were BPL (best planes) by W. E. Hunter and ORTEP (thermal ellipsoid plots) by C. K. Johnson.

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Table II. Fractional Atomic Coordinates for Compound 3^a

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--------|------------|------------|-------------|-------|------------|------------|------------|
| Ir(1) | 0.2288 (1) | 0.0271 (1) | 0.57926 (3) | C(7) | 0.172 (4) | -0.041 (4) | 0.533 (1) |
| Ir(2) | 0.2814 (1) | 0.2431 (1) | 0.56687 (3) | C(8) | 0.294 (4) | -0.072 (3) | 0.538 (1) |
| Ir(3) | 0.3661 (1) | 0.1133 (1) | 0.81700 (4) | C(9) | 0.332 (4) | -0.195 (4) | 0.551 (1) |
| Ir(4) | 0.1937 (1) | 0.2692 (1) | 0.81284 (3) | C(10) | 0.315 (4) | -0.229 (4) | 0.581 (1) |
| O(1) | -0.082 (2) | 0.042 (3) | 0.5948 (7) | C(11) | 0.246 (2) | -0.144 (2) | 0.6011 (7) |
| O(2) | -0.130 (2) | 0.090 (3) | 0.5455 (7) | C(12) | 0.127 (3) | -0.124 (3) | 0.5939 (9) |
| O(3) | -0.032 (3) | 0.352 (3) | 0.5254 (8) | C(13) | 0.057 (3) | -0.187 (3) | 0.565 (1) |
| O(4) | -0.035 (3) | 0.354 (3) | 0.5761 (7) | C(14) | 0.068 (4) | -0.153 (4) | 0.531 (1) |
| O(5) | 0.254 (4) | -0.112 (3) | 0.862 (1) | C(15) | 0.366 (4) | 0.241 (4) | 0.522 (1) |
| O(6) | 0.107 (3) | -0.139 (3) | 0.826 (1) | C(16) | 0.246 (4) | 0.265 (4) | 0.513 (1) |
| O(7) | -0.079 (3) | 0.057 (4) | 0.8137 (8) | C(17) | 0.214 (4) | 0.383 (4) | 0.500 (1) |
| O(8) | 0.003 (3) | 0.113 (3) | 0.8635 (8) | C(18) | 0.224 (4) | 0.484 (4) | 0.525 (1) |
| N(1) | 0.224 (2) | 0.121 (2) | 0.6192 (6) | C(19) | 0.271 (3) | 0.443 (3) | 0.5646 (8) |
| N(2) | 0.252 (2) | 0.234 (2) | 0.6143 (6) | C(20) | 0.384 (4) | 0.422 (3) | 0.5702 (9) |
| N(3) | 0.414 (2) | 0.047 (2) | 0.5931 (6) | C(21) | 0.479 (4) | 0.415 (4) | 0.545 (1) |
| N(4) | 0.442 (3) | 0.159 (3) | 0.5881 (7) | C(22) | 0.471 (4) | 0.309 (4) | 0.524 (1) |
| N(5) | 0.349 (3) | 0.176 (3) | 0.8617 (8) | C(23) | 0.387 (4) | 0.158 (4) | 0.892 (1) |
| N(6) | 0.264 (2) | 0.255 (2) | 0.8601 (6) | C(24) | 0.322 (4) | 0.228 (4) | 0.913 (1) |
| N(7) | 0.447 (3) | 0.271 (3) | 0.8135 (8) | C(25) | 0.246 (3) | 0.291 (3) | 0.8903 (8) |
| N(8) | 0.370 (4) | 0.359 (4) | 0.805 (1) | C(26) | 0.558 (5) | 0.327 (4) | 0.813 (1) |
| CA(1) | 0.069 (3) | 0.107 (3) | 0.5674 (9) | C(27) | 0.532 (5) | 0.444 (5) | 0.814 (1) |
| CA(2) | 0.095 (3) | 0.230 (3) | 0.5562 (7) | C(28) | 0.410 (4) | 0.468 (4) | 0.811 (1) |
| CA(3) | -0.052 (3) | 0.077 (3) | 0.5706 (8) | C(29) | 0.411 (4) | 0.102 (4) | 0.768 (1) |
| CA(4) | -0.253 (4) | 0.054 (3) | 0.548 (1) | C(30) | 0.327 (4) | 0.008 (4) | 0.773 (1) |
| CA(5) | 0.002 (3) | 0.309 (3) | 0.5516 (9) | C(31) | 0.367 (5) | -0.112 (5) | 0.777 (1) |
| CA(6) | -0.133 (5) | 0.445 (5) | 0.572 (1) | C(32) | 0.442 (5) | -0.132 (5) | 0.809 (1) |
| CA(7) | 0.223 (2) | 0.036 (2) | 0.8315 (5) | C(33) | 0.476 (4) | -0.049 (4) | 0.833 (1) |
| CA(8) | 0.129 (4) | 0.102 (4) | 0.818 (1) | C(34) | 0.554 (4) | 0.052 (4) | 0.831 (1) |
| CA(9) | 0.192 (5) | -0.071 (4) | 0.838 (1) | C(35) | 0.621 (5) | 0.036 (5) | 0.799 (1) |
| CA(10) | 0.094 (6) | -0.247 (6) | 0.844 (1) | C(36) | 0.547 (4) | 0.076 (4) | 0.768 (1) |
| CA(11) | 0.007 (4) | 0.080 (4) | 0.837 (1) | C(37) | 0.170 (5) | 0.314 (5) | 0.759 (1) |
| CA(12) | -0.113 (4) | 0.076 (4) | 0.873 (1) | C(38) | 0.083 (4) | 0.231 (4) | 0.766 (1) |
| C(1) | 0.205 (3) | 0.114 (3) | 0.6503 (8) | C(39) | -0.051 (4) | 0.277 (4) | 0.766 (1) |
| C(2) | 0.236 (3) | 0.217 (3) | 0.6663 (9) | C(40) | -0.086 (5) | 0.323 (4) | 0.797 (1) |
| C(3) | 0.260 (3) | 0.284 (3) | 0.6425 (9) | C(41) | 0.023 (4) | 0.363 (3) | 0.823 (1) |
| C(4) | 0.512 (4) | 0.000 (3) | 0.609 (1) | C(42) | 0.111 (5) | 0.437 (5) | 0.816 (1) |
| C(5) | 0.599 (4) | 0.089 (4) | 0.615 (1) | C(43) | 0.097 (5) | 0.511 (5) | 0.785 (1) |
| C(6) | 0.557 (3) | 0.185 (3) | 0.6021 (8) | C(44) | 0.145 (5) | 0.442 (4) | 0.756 (1) |

^aCoordinates of both crystallographically distinct molecules of the asymmetric unit are given. The labeling scheme of the lower numbered molecule may be seen in Figure 1. The other molecule is similarly labeled.

metrical alkynes (2 and 3) a pair of triplets near δ 6 is accompanied by two doublets at somewhat higher frequency (i.e., downfield), the four signals exhibiting a 1:1:2:2 intensity ratio. Such a pattern is consistent with a symmetry relationship perpendicular to the Ir₂ axis, whereby the two H⁴ resonances are distinguished because the pz bridging systems are nonequivalent although in each the H³ and H⁵ environments are identical. NMR spectroscopy (¹H or ¹⁹F) further establishes that in each adduct the two alkyne substituents R are symmetry-related since single resonances are observed for CF₃ or CH₃ (ester), respectively. These observations rule out any solution structure in which the twofold symmetry⁵ of the starting complex 1 is preserved, militating against perpendicular alkyne coordination (B) and suggesting a parallel-type geometry (A) which is unsymmetrical in the sense that the two heterocyclic bridging ligands are differently situated.

In the ¹H NMR spectrum (250 MHz) of the MPL adduct 4 all six hydrogens of the pz groups are distinguished, indicating that coordination of this alkyne to complex 1 removes all symmetry elements present¹ in molecules of the latter. This is confirmed by the resolution of eight methyne multiplets in the δ 3.5–5.8 range, signalling inequivalence of the two terminal diolefin ligands and implying an enantiomeric configuration resulting from parallel attachment of MPL as in A. The ester methyl resonance is observed at δ 3.66, i.e., identical in shift with that of coordinated DMAD in compound 3, while the alkynyl hydrogen gives rise to a singlet at conspicuously high frequency (δ 8.76). The ¹³C NMR spectrum of complex

4 provides even more persuasive evidence for the absence of any molecular symmetry since 24 signals are discernible for the 26 carbon atoms in the structure; the two C=C carbon atoms show shifts of 101.0 and 115.3 ppm with the single Me resonance at δ 51.2. The spectroscopic data therefore establish that MPL adopts a parallel orientation (type A) but offer no distinction between symmetrical coordination like that in compounds 2 and 3 and a less regular geometry resulting from unequal ligation by the different alkynyl carbon centers. Our interest in this distinction led us to complete a structural comparison between the three adducts using X-ray crystallography. In this context we note the very recent report of addition of MPL to a diiridium "A-frame" derivative,¹⁵ apparently providing the only previous example of complexation by this alkyne to give a bridged structure in which a dimetalated olefin structure was proposed on the basis of spectral data.

Alkyne addition paralleling that represented by eq 1 to the carbonyl phosphine analogue⁷ [Ir(CO)(PPh₃)(μ -pz)]₂ (5) of 1 was found to occur only with DMAD, yielding a further adduct (6). With MPL no reaction was observed under the mild conditions employed. With HFB, polymerization of the substrate acetylene was evident resembling that⁸ induced by PPh₃ alone; this suggests that free phosphine may be present in solution via release from compound 5, implying lability for which we have other

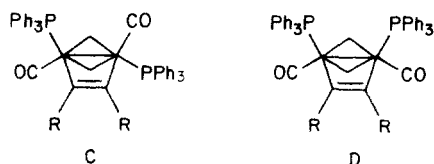
(15) Mague, J. T.; Klein, C. L.; Majeste, R. J.; Stevens, E. D. *Organometallics* 1984, 3, 1860.

Table III. Fractional Atomic Coordinates and Temperature Parameters for Compound 4^a

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> _{eq} , Å ² |
|-------|------------|------------|------------|---|
| Ir(1) | 21061 (6) | 23985 (5) | 86198 (7) | 426 (3) |
| Ir(2) | -3068 (6) | 28135 (4) | 77700 (6) | 406 (3) |
| O(1) | 3984 (12) | 4210 (12) | 12101 (15) | 94 (7) |
| O(2) | 2437 (11) | 3612 (10) | 12972 (11) | 68 (5) |
| N(1) | 2176 (11) | 3918 (10) | 7947 (13) | 44 (5) |
| N(2) | 952 (12) | 4133 (10) | 7497 (13) | 45 (5) |
| N(3) | 1195 (14) | 1953 (10) | 6267 (14) | 56 (6) |
| N(4) | -25 (12) | 2181 (10) | 5832 (13) | 48 (5) |
| C(1) | 3027 (18) | 4822 (12) | 7852 (18) | 57 (7) |
| C(2) | 2305 (17) | 5602 (13) | 7321 (18) | 56 (8) |
| C(3) | 955 (17) | 5145 (12) | 7100 (18) | 58 (8) |
| C(4) | 1484 (20) | 1762 (14) | 4985 (20) | 71 (9) |
| C(5) | 390 (21) | 1849 (17) | 3761 (22) | 82 (10) |
| C(6) | -547 (20) | 2131 (14) | 4327 (20) | 75 (9) |
| C(7) | 639 (14) | 3417 (11) | 10007 (17) | 46 (6) |
| C(8) | 1887 (14) | 3220 (12) | 10437 (16) | 49 (6) |
| C(9) | 2905 (16) | 3712 (13) | 11876 (19) | 53 (7) |
| C(10) | 3349 (21) | 4126 (18) | 14476 (20) | 88 (10) |
| C(11) | 1827 (16) | 654 (13) | 8680 (23) | 64 (8) |
| C(12) | 2117 (17) | 1137 (14) | 10097 (21) | 62 (8) |
| C(13) | 3389 (21) | 1175 (15) | 11347 (24) | 88 (10) |
| C(14) | 4660 (19) | 1974 (20) | 11271 (25) | 97 (12) |
| C(15) | 4291 (16) | 2566 (13) | 9893 (21) | 59 (8) |
| C(16) | 3963 (15) | 2132 (15) | 8385 (25) | 79 (9) |
| C(17) | 3942 (19) | 896 (15) | 8020 (28) | 91 (11) |
| C(18) | 2767 (21) | 137 (15) | 8110 (24) | 81 (10) |
| C(21) | -1588 (15) | 1241 (12) | 7446 (18) | 53 (7) |
| C(22) | -1389 (15) | 1765 (14) | 8901 (20) | 64 (8) |
| C(23) | -2366 (18) | 2300 (14) | 9327 (21) | 67 (8) |
| C(24) | -2460 (16) | 3467 (16) | 8938 (18) | 66 (8) |
| C(25) | -1812 (14) | 3765 (14) | 7785 (18) | 55 (7) |
| C(26) | -2192 (17) | 3230 (15) | 6391 (18) | 62 (8) |
| C(27) | -3357 (18) | 2196 (16) | 5778 (21) | 80 (9) |
| C(28) | -2883 (18) | 1155 (15) | 6115 (20) | 72 (8) |

^a Estimated standard deviations are given in parentheses. Coordinates $\times 10^4$ where $n = 5$ for Ir and $n = 4$ otherwise. Temperature parameters $\times 10^3$ where $n = 4$ for Ir and $n = 3$ otherwise. U_{eq} = the equivalent isotropic temperature parameter. $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i^* a_j^*)$. Primed values indicate that U_{iso} is given. $T = \exp[-(8\pi^2 U_{iso} \sin^2 \theta) / \lambda^2]$.

evidence¹⁶ and which may be significant in relation to catalytic properties. The ¹H NMR spectrum of compound 6 includes two ester methyl resonances (δ 3.08, 3.12); four pz proton signals are clearly resolved with a further two partially obscured⁷ by the PPh₃ envelope, while in the IR there are two ν (CO) bands (1990 vs. 2021 w cm⁻¹). These data are important in that they imply a geometry for the DMAD adduct 6 derived directly from the trans disposition⁷ of terminal ligands in 5 without stereochemical reorganization at Ir, i.e., schematically configuration C rather than D.



The molecular geometry of the HFB addition product 2 has been illustrated as an ORTEP plot in ref 4, in which were also listed crystal data together with full details of the structure determination as supplementary material. Final fractional coordinates for compounds 3 and 4 are set out in Tables II and III, respectively, and the two molecules are compared in parts a and b of Figure 1. Two marginally different molecules occupy the asymmetric unit in crystals of compound 3. Important bond distances and

Table IV. Important Bond Lengths (Å) and Angles (deg)

| Compound 3 | | | |
|-------------------|------------|--------------------|------------|
| Bond Lengths | | | |
| Ir(1)-N(1) | 2.00 (3) | Ir(1)-N(3) | 2.10 (2) |
| Ir(2)-N(2) | 2.07 (2) | Ir(2)-N(4) | 2.14 (3) |
| Ir(3)-N(5) | 2.05 (3) | Ir(3)-N(7) | 2.05 (3) |
| Ir(4)-N(6) | 2.04 (3) | Ir(4)-N(8) | 2.30 (4) |
| Ir(1)-C(7) | 2.10 (4) | Ir(1)-C(8) | 2.29 (4) |
| Ir(1)-C(11) | 2.18 (3) | Ir(1)-C(12) | 2.23 (4) |
| Ir(2)-C(15) | 2.22 (4) | Ir(2)-C(16) | 2.26 (5) |
| Ir(2)-C(19) | 2.31 (3) | Ir(2)-C(20) | 2.36 (4) |
| Ir(3)-C(29) | 2.20 (4) | Ir(3)-C(30) | 2.20 (4) |
| Ir(3)-C(33) | 2.29 (5) | Ir(3)-C(34) | 2.24 (4) |
| Ir(4)-C(37) | 2.29 (5) | Ir(4)-C(38) | 2.24 (4) |
| Ir(4)-C(41) | 2.31 (4) | Ir(4)-C(42) | 2.16 (6) |
| Ir(1)-CA(1) | 2.03 (4) | Ir(2)-CA(2) | 2.10 (3) |
| Ir(3)-CA(7) | 2.02 (2) | Ir(4)-CA(8) | 2.08 (4) |
| Ir(1)-Ir(2) | 2.633 (2) | Ir(3)-Ir(4) | 2.642 (2) |
| Bond Angles | | | |
| N(1)-Ir(1)-N(3) | 82 (1) | N(2)-Ir(2)-N(4) | 79 (1) |
| N(1)-Ir(1)-CA(1) | 80 (1) | N(3)-Ir(1)-CA(1) | 147 (1) |
| N(2)-Ir(2)-CA(2) | 85 (1) | N(4)-Ir(2)-CA(2) | 146 (1) |
| Ir(1)-N(1)-N(2) | 111 (2) | Ir(1)-N(1)-C(1) | 144 (2) |
| Ir(2)-N(2)-N(1) | 105 (2) | Ir(2)-N(2)-C(3) | 148 (2) |
| Ir(1)-N(3)-N(4) | 108 (2) | Ir(1)-N(3)-C(4) | 146 (2) |
| Ir(2)-N(4)-N(3) | 107 (2) | Ir(2)-N(4)-C(6) | 140 (2) |
| Ir(1)-CA(1)-CA(2) | 107 (2) | Ir(1)-CA(1)-CA(3) | 134 (3) |
| Ir(2)-CA(2)-CA(1) | 103 (2) | Ir(2)-CA(2)-CA(5) | 135 (2) |
| N(5)-Ir(3)-N(7) | 82 (1) | N(6)-Ir(4)-N(8) | 87 (1) |
| N(5)-Ir(3)-CA(7) | 72 (1) | N(7)-Ir(3)-CA(7) | 143 (1) |
| N(6)-Ir(4)-CA(8) | 86 (1) | N(8)-Ir(4)-CA(8) | 139 (2) |
| Ir(3)-N(5)-N(6) | 111 (2) | Ir(3)-N(5)-C(23) | 142 (3) |
| Ir(4)-N(6)-N(5) | 106 (2) | Ir(4)-N(6)-C(25) | 142 (2) |
| Ir(3)-N(7)-N(8) | 114 (3) | Ir(3)-N(7)-C(26) | 144 (3) |
| Ir(4)-N(8)-N(7) | 100 (3) | Ir(4)-N(8)-C(28) | 132 (4) |
| Ir(3)-CA(7)-CA(8) | 104 (2) | Ir(3)-CA(7)-CA(9) | 136 (3) |
| Ir(4)-CA(8)-CA(7) | 107 (3) | Ir(4)-CA(8)-CA(11) | 120 (3) |
| Compound 4 | | | |
| Bond Lengths | | | |
| Ir(1)-Ir(2) | 2.638 (1) | Ir(2)-N(2) | 2.071 (11) |
| Ir(1)-N(1) | 2.050 (12) | Ir(2)-N(4) | 2.141 (12) |
| Ir(1)-N(3) | 2.146 (13) | Ir(2)-C(7) | 2.088 (15) |
| Ir(1)-C(8) | 2.100 (15) | Ir(2)-C(21) | 2.171 (14) |
| Ir(1)-C(11) | 2.173 (16) | Ir(2)-C(22) | 2.211 (15) |
| Ir(1)-C(12) | 2.190 (17) | Ir(2)-C(25) | 2.197 (15) |
| Ir(1)-C(15) | 2.253 (16) | Ir(2)-C(26) | 2.203 (17) |
| Ir(1)-C(16) | 2.205 (14) | | |
| Bond Angles | | | |
| N(3)-Ir(1)-N(1) | 80.9 (5) | N(4)-Ir(2)-N(2) | 79.9 (4) |
| C(8)-Ir(1)-N(1) | 81.5 (5) | C(7)-Ir(2)-N(2) | 82.7 (5) |
| C(8)-Ir(1)-N(3) | 143.1 (6) | C(7)-Ir(2)-N(4) | 144.7 (5) |
| N(2)-N(1)-Ir(1) | 108.6 (8) | N(4)-N(3)-Ir(1) | 107.8 (9) |
| C(1)-N(1)-Ir(1) | 143.2 (11) | C(4)-N(3)-Ir(1) | 142.6 (12) |
| N(1)-N(2)-Ir(2) | 108.1 (8) | N(3)-N(4)-Ir(2) | 107.3 (9) |
| C(3)-N(2)-Ir(2) | 140.9 (11) | C(6)-N(4)-Ir(2) | 140.6 (13) |
| C(8)-C(7)-Ir(2) | 107.3 (11) | C(7)-C(8)-Ir(1) | 108.3 (11) |

angles are listed in Table IV. As inferred from the spectroscopic measurements in all three adducts the alkyne bridges the two metal centers in a parallel-bound arrangement (A). More strikingly and perhaps surprisingly coordination of MPL is quite regular, with half of the molecule of 4 virtually superimposable on the configuration of 3 (Figure 1). In each case the acetylene has added beneath the Ir₂ vector resulting in η^2 ligation which has the effect of pushing the pz bridging ligands back into inequivalent positions. In 2 and 3 a plane of symmetry in a direction perpendicular to the intermetallic axis is broken only by the orientation of the CO₂Me groups (which will be able to rotate in solution) but in 4 no symmetry remains. Thus in 2 and 3 the COD ring systems are symmetric related with each rotated away from the alkyne substituents to generate a highly distorted octahedral en-

(16) Including replacement of P(C₆H₅)₃ by P(C₆D₅)₃ during addition of H₂ to complex 6: Stobart, S. R.; Vefghi, R., unpublished observations.

Table V. Structural Comparison of Bridging Pyrazolyl Geometry in Diiridium Complexes

| compound | M-N, Å | M-N-C, deg | M-N-N, deg | M-M | ref |
|---|--------------------------------------|------------|------------|-----------|-----|
| [Ir(DPM)(μ -pz)] ₂ ^{a,b} | 2.09 | 131 | 121 | 3.506 (1) | 18 |
| [Ir(COD)(μ -pz)] ₂ ^b | 2.081 (8) | 136.2 (8) | | 3.216 (1) | 5 |
| [Ir(PPh ₃)(CO)(μ -pz)] ₂ ^b | 2.08 | 137 | 116 | 3.162 (2) | 7 |
| [Ir ₂ (COD) ₂ (μ -pz) ₂ (Me)(I)] ^c | 2.08 | 136 | 115 | 3.112 (1) | 4 |
| [Ir(COD)(μ -fpz)] ₂ ^{b,d} | 2.08 | 137 | 115 | 3.073 (1) | 5 |
| [Ir(PPh ₃)(CO)(μ -4-Cl-pz)(Cl)] ₂ ^{c,e} | 2.07 | 139 | 109 | 2.737 (1) | 7 |
| 2 ^c | 2.18, ^f 2.12 ^g | 142 | 107 | 2.623 (2) | 4 |
| 3 ^c | 2.15, ^f 2.04 ^g | 142 | 108 | 2.64 | h |
| 4 ^c | 2.14, ^f 2.06 ^g | 143 | 108 | 2.638 (1) | h |

^aDPM = bis(diphenylphosphino)methane. ^bIr(I) dimer. ^cIr(II) dimer. ^dfpz = 3,5-bis(perfluoromethyl)pyrazolyl. ^eCl-pz = 4-chloropyrazolyl. ^fTrans to acetylene. ^gTrans to alkene. ^hThis work.

environment at each Ir center with the adjacent metal atom taking up the sixth coordination site. In molecules of 4 a similar operation renders the two COD ligands inequivalent as is demonstrated in solution by both ¹H and ¹³C NMR data.

In all three complexes the two metal centers are within bonding distance, 2.623 (2), 2.638 (mean), and 2.637 (1) Å for 2, 3, and 4, respectively, contracted considerably from 3.216 Å in compound 1. Metal-metal approach is accommodated by the COD rotation with substrate occupation of equatorial, rather than axial, sites at Ir with the overall configuration conforming to that which would be predicted on the basis of diiridium(II) d⁷-d⁷ spin pairing by Ir₂ bond formation. This contrasts with two-center oxidative addition to compound 1 in which the two axial positions are substituted and steric opposition between the COD ligands controls the Ir₂ separation.^{1,4} Existence of Ir-Ir bonding in 2-4 is confirmed by the degree of strain imposed on both types of bridge geometry: Ir-C-C angles at the alkyne carbons are reduced to 103-107° from the idealized sp² structure (an effect similar to that attributed to Rh-Rh bonding in¹⁷ Rh₂Cl₂(μ -HFB)(μ -dpm)₂, 7 (dpm = (diphenylphosphino)methane)) and a corresponding compression in Ir-N-N angles is obvious from the values arranged in Table V. These distortions arise from Ir-Ir bond distances which are markedly shorter than those encountered in any related alkyne- (i.e., configuration A) or pyrazolyl-bridged binuclear complex (ref 2a; Table V). We have previously drawn attention to the remarkable way in which the pz heterocycle can accommodate major changes in bridging distance and Table V maps the progressive deviation from trigonal (i.e., sp²-type) angles at N (i.e., Ir-N-C, Ir-N-N) accompanying contraction along the Ir₂ vector.

Close inspection of the structure of compound 4 highlights a further interesting phenomenon. Although Ir-C distances from the two different carbon atoms of the unsymmetrical MPL bridge are almost identical, 2.100 (15) and 2.088 (15) Å, Ir-N distances to the two pyrazolyl units are quite different with one at 2.06 (mean) Å and the other at 2.14 Å. The longer bonds are those occupying a pseudotrans relationship with the alkyne while those trans to COD are normal, a difference which may be ascribed to the influence of the σ -bonded alkenyl carbon atom. This situation may be significant in relation to the bridge replacement which occurs⁶ on addition of HFB to Ir₂(COD)₂(μ -pz)(μ -fpz), fpzH = 3,5-bis(trifluoromethyl)pyrazole. In accord with the diiridacyclobutene formalism A the carbon-carbon distances in the μ -C₂R¹R² unit (range 1.31-1.40 Å) approximate to those expected for C=C; the geometry of the HFB fragment matches almost exactly that found in compound 7. By contrast with the situation observed in DMAD adducts of two different dpm-bridged diiridium complexes^{15,19} the ester groups in compound 3 oppose one another more or less directly across the Ir₂ (and C₂) vector suggesting that the relative orientation is controlled by packing forces.

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Registry No. 1, 89710-83-8; 2, 98394-10-6; 3, 98394-11-7; 4, 98394-12-8; 6, 98394-13-9; HFB, 692-50-2; DMAD, 762-42-5; MPL, 922-67-8; [Ir(CO)(PPh₃)(M-pz)]₂, 98420-38-3.

Supplementary Material Available: Tables of structure factor amplitudes, bond distances and angles, and anisotropic temperature factors (48 pages). Ordering information is given on any current masthead page.

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