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Registry No. 1, 80461-91-2; **2**, 80461-90-1; **3**, 80471-11-0; **4**, 80462-17-5; $[(PPh_3)(CO)Ir(H)(\mu\text{-pz})]_2$, 80462-16-4; $[(PPh_3)(CO)Ir(Br)(\mu\text{-pz})]_2$, 80462-15-3; $[(PPh_3)(CO)Ir(I)(\mu\text{-pz})]_2$, 80462-14-2; $[(COD)Ir(\mu\text{-pz})]_2$, 80462-13-1; $[(COD)IrCl]_2$, 12112-67-3; *trans*-$Ir(PPh_3)_2(CO)(Cl)$, 15318-31-7.

Supplementary Material Available: Final fractional coordinates and thermal parameters for **1** and **2** as well as bond lengths and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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[21] Herrmann, W. A.; Plank, J.; Riedel, R.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63.

Pyrazolyl-Bridged Iridium Dimers. 2. Contrasting Modes of Two-Center Oxidative Addition to a Bimetallic System and Reductive Access to the Starting Complex: Three Key Diiridium Structures Representing Short Nonbonding and Long and Short Bonding Metal-Metal Interactions

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Transition-metal catalyzed homogeneous reactions frequently depend on sequential oxidative addition/reductive elimination cycles which access two different oxidation states for the metal site. While numerous examples of such behavior occurring at a single coordinately unsaturated metal center exist, only quite recently has attention been focused specifically[1] on polymetallic systems which can accommodate similar chemistry without fragmentation, leading to intermediacy of mononuclear reactive species. The objective in this context is to explore the relevance of polymetal cluster complexes as models for the activity of metal surfaces in high-energy heterogeneous catalytic interconversions.[2] Pursuing our interest in reactions requiring participation of both metal atoms in a simple dimer compound,[3] we here compare two different modes of two-center oxidative addition at the same iridium(I) configuration; each leads to metal-metal bond formation to give a diamagnetic (formally) iridium(II) product. But the Ir-Ir distances so adopted approach opposite extremes although the integrity of the binuclear unit is maintained by the same bridging ligand. We also demonstrate that the reverse transformation, i.e., reduction of both metal centers, can be brought about, again without disruption of the dimer.

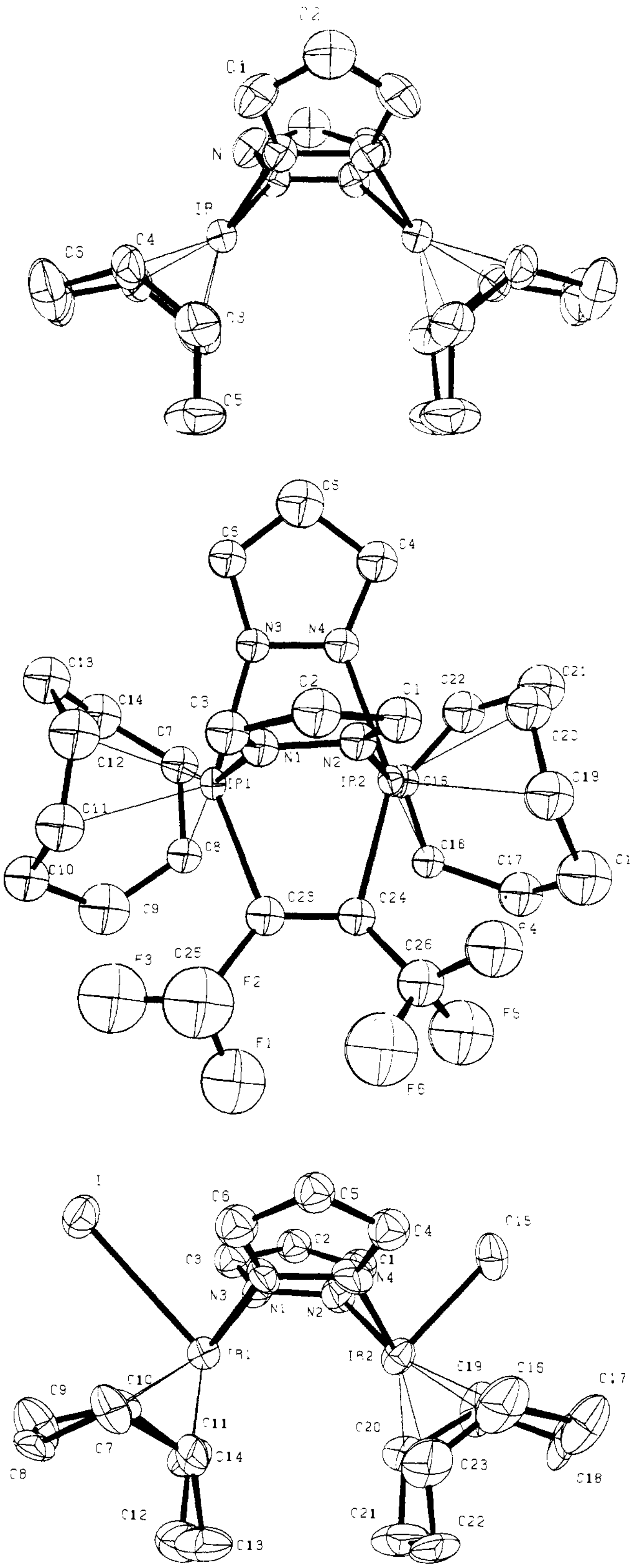

Figure 1. Molecular structures of bis(cyclooctadiene)di-μ-pyrazolyl-diiridium (a) and its adducts with hexafluorobut-2-yne (b) and methyl iodide (c).

The structure of the bis(cyclooctadiene)-di-μ-pyrazolyl-diiridium dimer[4] (**1**), isolated as deep purple crystals from the reaction of $[(COD)IrCl]_2$ with pyrazole/triethylamine,[3] is represented in Figure 1a. The geometry of the molecule resembles that of the

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[1] Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871 and references therein. Geoffroy, G. L.; Gladfelter, W. L. *Adv. Organomet. Chem.* **1980**, *18*, 207, Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489.

[2] Ford, P. C.; Ungermann, C.; Laudis, V.; Moya, S. A.; Riuber, R. C.; Laine, R. H. "Inorganic Compounds with Unusual Properties"; *Adv. Chem. Ser.* **1979**, No. *173*, 225. Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.

[3] Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J., preceding communication.

0002-7863/82/1504-0922$01.25/0

related (triphenylphosphine)(carbonyl)iridium(I) compound[3] (**2**) in that the bridging framework is bent into a deep boat conformation in which the metal atoms are separated by only 3.216 Å. The unusually short distances between the (formally) nonbonded, 16-electron Ir centers in these two complexes suggest that they belong to a further class of compounds exhibiting a weak ground-state metal–metal interaction,[5] and accordingly, together with several other members of the same family, they are currently the subject of a comprehensive spectroscopic investigation.[6] The COD ligands in **1** are symmetrically bound as normal chelating diolefins.

Addition of hexafluorobut-2-yne, dmad, or *o*-chloranil to compound **1** in THF leads to slow formation (12 h) of pale yellow to white 1:1 adducts[7] of **3**–**5**, respectively. By contrast with X_2 (X = Br or I) or MeI the reaction mixture immediately darkens under similar conditions, affording deep brown (Br) or purple 1:1 adducts, **6**–**8**. Reactions with 2 equiv of X_2 in THF yields dark 2:1 adducts, the structure of which is as yet unknown. Reaction of **7** at ambient temperature in THF with Na/Hg, Na/naphthalene, or $Tl(C_5H_5)$ smoothly regenerates complex **1**. Reaction of **7** or **8** with MeMgBr in Et_2O/THF results in quantitative formation of the orange-red $Me_2[(COD)Ir(Me)(\mu\text{-}pz)]_2$ (**9**). ^1H NMR spectra of compounds **6**–**8** show a monotonic upfield shift in resonances due to pyrazolyl protons with τ_{Me} for **8** and **9** at 8.49. These reactions represent two distinct modes of two-center oxidative addition, each of which has been further characterized by single-crystal X-ray crystallography and confirm that subsequent reduction is possible while preserving the link between the neighboring metal sites.

Complex **3** was obtained as colorless crystals.[8] The structure is shown in Figure 1b. The acetylene has effectively oxidatively added across the two Ir(I) centers to give a 1,2-dimetallosubstituted ethene, the terminal bidentate COD groups twisting somewhat to avoid contact with the CF_3 substituents. The pyrazolyl-bridged boat configuration is thus capped to give a tricyclic core in which the Ir—Ir bond at 2.623 (2) Å is nearly as short as that (2.554 Å) attributed[9] to an Ir=Ir interaction in $[Ir(CO)(PPh_3)(\mu\text{-}PH_2)]_2$, much more so than in a $C_2(CF_3)_2$-bridged nitrosyldiiridium species,[10] although the Ir_2 separation in the latter (2.84 Å)[11] was not considered in assigning an oxidation number of +1 to the metal atoms. Identification of the ethenyl bridge parallel to the intermetal axis in **3** with C^{23}–C^{24} = 1.31 Å supports the structure speculated[12] for the corresponding adduct of a related *tert*-butylthiolato-bridged Ir dimer. By complete contrast, $CF_3C{:}CCF_3$ adds to each metal center in $[(COD)IrCl]_2$ as a η^1-vinyl with transfer of one H to the COD ligand, giving an allylvinylchloro-bridged[13] Ir(III) dimer with intermetallic distance 3.79 Å.

The molecular structure of compound **8**, isolated as purple-black crystals,[14] is very different as shown in Figure 1c. Indeed, oxidative addition has perturbed the geometry of **1** (Figure 1a) very little. Attachment of a methyl group to one Ir center (Ir^2–C^{15} = 2.21 Å) together with an iodide ligand to the other (Ir^1–I = 2.961 Å) is accompanied by contraction of the interiridium distance from 3.216 (1) to 3.112 (1) Å. Interpretation of the latter as a very long Ir–Ir single bond is required by the diamagnetism of the product,[15] although it exceeds the (formally) nonbonded distance in one of the unoxidized Ir(I) dimers (see ref 10, preceding communication) by ca. 0.05 Å; this may be the result of inductive electron donation to the metal in **8**, contrasting with contraction of the orbitals involved in bonding between the Ir(II) centers through release onto the electron-poor ethenyl bridge in **3** or by electron withdrawal in the chlorine adduct[3] of compound **2**. Finally we note that **8** appears to be the first crystallographically substantiated example of 1,2 addition of an alkyl halide across two adjacent metal atoms[16] and that the combination of a long Ir–Ir bond in systems like **8** and a short Ir_2 distance in dimers like **1** may favor facile redox chemistry of a very significant type. Further synthetic, structural, and electrochemical studies are in progress.

Acknowledgment. We thank the N.S.E.R.C. (Canada), the University of Victoria, and the National Science Foundation (J.L.A.) for financial support of this research.

Supplementary Material Available: Final fractional coordinates, thermal parameters, and bond lengths and angles for **1**, **3**, and **8** (9 pages). Ordering information is given on any current masthead page.

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(4) Crystal Data for **1**: $C_{22}H_{30}Ir_2N_4$; M = 734.9; orthorhombic; space group *Cmcm*; a = 12.750 (4), b = 12.037 (4), c = 13.432 (4) Å; V = 2061.4 Å^3; Z = 4; ρ(calcd) = 2.37 g cm^{-3}; Mo Kα radiation, λ = 0.71069 Å; Nonius CAD4 diffractometer; R = 0.022 for 473 observed reflections have $F_o^2 > 3\sigma(F_o^2)$. Parameters relevant to data collection and reduction are referenced in the previous paper and are the same for all three structures reported herein.

(5) Mann, K. R.; Gray, H. B. "Inorganic Compounds with Unusual Properties"; *Adv. Chem. Ser.* **1979**, *No. 173*, 225. Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *No. 102*, 6761 and references therein.

(6) In collaboration with H. B. Gray, S. F. Rice, and T. D. Smith.

(7) Confirmatory analytical data were obtained in each instance; dmad = dimethylacetylenedicarboxylate. Adducts of *o*-chloranil with mononuclear iridium(I) compounds have been reported previously: Smith, L. R.; Blake, D. M.; Jackson, D. *J. Organomet. Chem.* **1978**, *159*, 409, Sohn, Y. S.; Balch, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 1144.

(8) Crystal data for **3**: $C_{29}H_{36}F_6Ir_2N_4$; M = 939.0; monoclinic; space group $P2_1/n$; a = 11.347 (4), b = 18.415 (6), c = 14.087 (4) Å; β = 111.29 (4)°; V = 2742.7 Å^3; Z = 4; ρ(calcd) = 2.27 g cm^{-3}; Mo Kα, λ = 0.71069 Å; Nonius CAD4 diffractometer; R = 0.048 for 1510 independent reflections with $F_o^2 > 3\sigma(F_o^2)$.

(9) Mason, R.; Søtofte, I.; Robinson, S. D.; Uttley, M. F. *J. Organomet. Chem.* **1972**, *46*, C61.

(10) Clemens, J.; Green, M.; Miug-Cheng, K.; Fritchie, C. J.; Mague, J. T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 53.

(11) Fritchie, C. J., private communication.

(12) Devillers, J.; Bonnet J.-J.; de Montanzon, D.; Galy, J.; Poiblanc, R. *Inorg. Chem.* **1980**, *19*, 154.

(13) Russell, D. R.; Tucker, P. A. *J. Organomet. Chem.* **1977**, *125*, 303.

(14) Crystal data for **8**: $C_{23}H_{33}IIr_2N_4$; M = 876.9; monoclinic; space group $P2_1/n$; a = 11.156 (4), b = 16.242 (5), c = 13.127 (4) Å; β = 96.52 (4)°; V = 2363.2 Å^3; Z = 4; ρ(calcd) = 2.46 g cm^{-3}; Mo Kα radiation, λ = 0.71069 Å; Nonius CAD4 diffractometer; R = 0.026 for 1306 independent reflections, $F_o^2 > 3\sigma(F_o^2)$.

(15) Solutions of this complex gave well-resolved NMR spectra showing no unusual shifts; no EPR signal was detectable to the limit of instrumental sensitivity.

(16) Lewis, N. S.; Mann, K. R.; Gordon, J. G.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461. Schmidbauer, H.; Mandl, J. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1976**, *109*, 466. Hermann, W. A.; Plank, J.; Reidel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63.