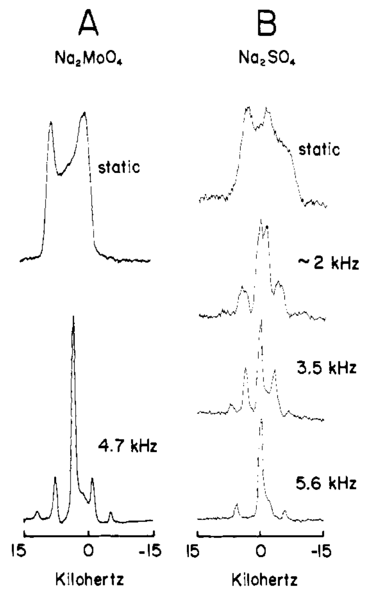

Figure 2. 95-MHz ^{23}Na Fourier transform NMR spectra of Na_2MoO_4 and Na_2SO_4. (A) Na_2MoO_4, static and spinning at 4.7 kHz and $\theta = 38°$; (B) Na_2SO_4, static and spinning at $\theta = 48°$ at the speeds indicated. Spectra were recorded on a home-built instrument operating with an 8.5-T, 3.0-in. bore, superconducting solenoid.

effective in reducing second-order quadrupole interactions. We show therefore in Figure 2A,B spectra of $^{23}Na_2MoO_4$ and $^{23}Na_2SO_4$ at 8.5 T (corresponding to a ^{23}Na resonance frequency of 95.2 MHz) for spinning speeds up to ~6 kHz. For the static samples, the line widths are reduced to ≈10–12 kHz upon increasing H_0 from 3.5 to 8.5 T. At low spinning speeds there are again spinning side bands, but for fast ($\gtrsim$3 kHz) rotation well-resolved center bands are obtained (Figure 2A,B) for both Na_2MoO_4 ($\eta = 0$) spinning at $\theta = 38°$ and for Na_2SO_4 ($\eta = 0.6$) spinning at $\theta = 48°$, although the lines are still asymmetric, and for the general case of an unknown e^2qQ/h, appropriate corrections to the observed shift cannot readily be made. These will, however, be of the order of the line width for e^2qQ/h of ~1–3 MHz and may be determined from frequency dependence studies. These results, together with those we have obtained on a variety of other nuclei having spins $I = {}^3/_2, {}^5/_2, {}^7/_2$, and ${}^9/_2$ (e.g., ^{11}B, ^{27}Al, ^{51}V, ^{55}Mn, and ^{93}Nb),[12,18] including the observation of fine structure in one system having $e^2qQ/h = 19.5$ MHz,[12] together with recent independent work on ^{27}Al by Muller et al.[19] and on ^{23}Na by Kundla et al.[20] using magic-angle (54.7°) spinning, strongly suggest that it is now possible to investigate a greatly increased number of nuclei in the periodic table in solid-state systems of chemical and biological interest. For high-resolution studies, the results of Figures 1 and 2 clearly indicate the need of operating at the highest field strengths possible ($\gtrsim$12 T) together with the need for development of ultra-high-speed variable-angle spinner assemblies; studies of a variety of organometallics (^{55}Mn, ^{95}Mo, ^{99}Ru), borates and boron hydrides (^{11}B), oxides (^{17}O), supported catalysts and zeolites (^{27}Al), and metalloprotein model systems (^{63}Cu, ^{67}Zn) are currently in progress.

Acknowledgment. We thank S-Y. Kang, D. Wright, and R. P. Skarjune for help with probe design and construction, T. Ray for help with carrying out experiments, and G. R. Hays, S. Vega, and J. P. Yesinowski for discussions. This work was supported in part by the U.S. National Institutes of Health (Grants HL-19481 and CA-00595) and the US National Science Foundation (Grants PCM 78-23021 and PCM 79-23170), and has benefited from use of facilities made available through the University of Illinois National Science Foundation Regional Instrumentation Facility (Grant CHE 79-16100).

Registry No. NaCl, 7647-14-5; $NaBrO_3$, 7789-38-0; Na_2MoO_4, 7631-95-0; Na_2SO_4, 15124-09-1.

---

(17) E. R. Andrew, *Int. Rev. Phys. Chem.*, **1**, 195 (1981).

(18) E. Oldfield, R. A. Kinsey, B. Montez, T. Ray and K. A. Smith, *J. Chem. Soc., Chem. Commun.*, in press.

(19) D. Muller, W. Gessner, H.-J. Behrens, and G. Scheler, *Chem. Phys. Lett.*, **79**, 59 (1981).

(20) E. Kundla, A. Samosan, and E. Lippmaa, *Chem. Phys. Lett.*, **83**, 229 (1981).

Pyrazolyl-Bridged Iridium Dimers. 1. Accommodation of Both Weak and Strong Metal–Metal Interactions by a Bridging Pyrazolyl Framework in Dissymmetric Dimeric Structures

Kathy A. Beveridge, Gordon W. Bushnell, Keith R. Dixon,
Donald T. Eadie, and Stephen R. Stobart*

Department of Chemistry, University of Victoria
British Columbia, Canada V8W 2Y2

Jerry L. Atwood and Michael J. Zaworotko

Department of Chemistry, University of Alabama
University, Alabama 35486

Received June 22, 1981

The chemistry of polynuclear transition-metal compounds has entered a phase of extremely rapid development, as a consequence of progressive rationalization of synthetic stragety as well as increased access to appropriate characterization techniques. This activity reflects a high level of interest in the influence of one another of neighboring metal centers, electronically in terms of excited-state phenomena[1] or electron delocalization between adjacent atoms[2] or chemically in relation to reactivity at (especially multiple) metal–metal bonds[3] and cooperative catalytic action, including efforts to substantiate a "cluster/surface" analogy.[4] Such effects will be manifested in their simplest form in dimeric complexes, principles established from which may be ultimately translated into the context of larger aggregates of metal atoms. We have commented recently[5] on the versatility of the η^2-pyrazolyl group as a bridging ligand, which can straddle an unusually wide range of intermetallic separations to hold two adjacent metal centers in a chemically extremely stable configuration. Here we show that the same linkage can absorb drastic contraction of a bridged framework, arising through metal–metal bond formation accompanying oxidation at each atom in a dimeric array. This has been identified during a systematic investigation of the structure and reactivity of a series of pyrazolyl-bridged iridium(I) complexes, a novel class of bimetallics, the chemistry of which combines a number of remarkable features.

Reaction between *trans*-$Ir(PPh_3)_2(CO)(Cl)$ (Vaska's complex) and pyrazolide anion (ambient, THF, 6 h) affords blood-red crystals of dicarbonylbis(triphenylphosphine)di-μ-pyrazolyl-di-iridium(I) (**1**) (30–60%), characterized by[6] single-crystal X-ray diffractometry (Figure 1). The same compound can be synthesized stepwise from $[(COD)IrCl]_2$ (COD = 1,5-cyclo-

---

(1) Kent, R. M.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462 and references therein.

(2) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *18*, 3369. Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374.

(3) Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871. Chisholm, M. H.; Haitko, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 6984. Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354.

(4) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(5) Stobart, S. R.; Dixon, K. R.; Eadie, D. T.; Atwood, J. L.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 931.

(6) Crystal data for **1**: $C_{44}H_{36}Ir_2N_4O_2P_2$; $M = 1099.1$; triclinic; space group $P\bar{1}$; $a = 9.992$ (4), $b = 10.402$ (4), $c = 20.278$ (8) Å; $\alpha = 90.01$ (4), $\beta = 90.10$ (4), $\gamma = 105.13$ (4)°; $V = 2037$ Å^3; $Z = 2$; ρ(calcd) = 1.79 g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; $R = 0.046$ for 1481 observed reflections, $F_0^2 > 3\sigma(F_0^2)$. An empirical absorption correction was applied. The method of data collection and computer library have been described previously: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 46.

0002-7863/82/1504-0920$01.25/0

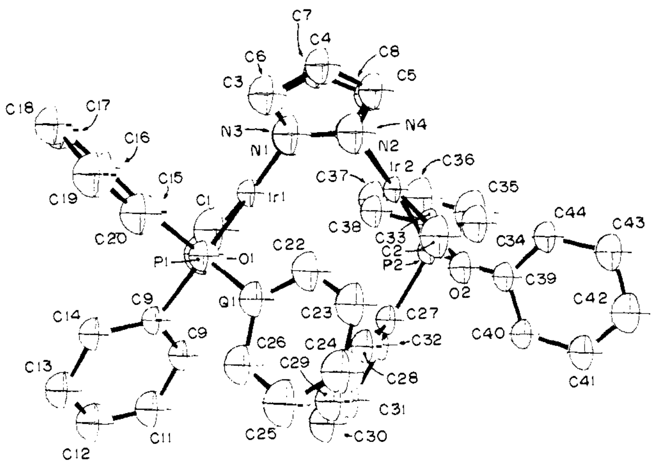

Figure 1. Molecular structure of $[Ir(CO)(PPh_3)(\mu\text{-pz})]_2$ (**1**). The full atomic labeling scheme is available (with the atomic position and thermal parameters) as supplementary material.

octadiene): treatment with pyrazole/triethylamine affords intensely purple $[(COD)Ir(\mu\text{-pz})]_2$ (pzH = pyrazole) whence displacement of COD with CO followed by reaction with PPh_3 gives compound **1** in ~85% yield. The latter route provides access to a family of related dimeric complexes, including those having alternate terminal ligands.

The geometric arrangement[7] in complex **1** places each pair of ligands (either CO or PPh_3) mutually trans across the metal–metal axis (Figure 1), resulting in a dissymmetric structure belonging to the molecular point-group C_2. NMR measurements (^1H and ^{31}P) indicate that the molecule is stereochemically rigid in solution and is therefore in principle resolvable. Chirality of this sort (i.e., not derived from ligand asymmetry) is presently confined to a very limited range of polynuclear metal complexes[8] and is of specific interest in relation to asymmetric induction catalysis.[9] However, the most surprising feature of the structure is the degree of fold in the six-membered cyclic core when it is bent into a boat conformation, which brings the two metal atoms to 3.162 (2) Å from one another; this distance is extraordinarily short by comparison with related complexes[5] incorporating exobidentate pyrazolyl bridges[10] and is consistent with some degree of metal–metal interaction as identified by Gray and co-authors in related "face-to-face" Rh(I) dimers.[11] Indeed in the structurally similar complex $[P(OMe)_3(CO)Ir(\mu\text{-S-}t\text{-Bu})]_2$ where the Ir centers are linked by single-atom bridges, the separation[12] is actually greater (3.22 Å) while in the rhodium analogue of **1**, structurally characterized very recently,[13] the intermetallic distance is very much longer at 3.57 Å.

Oxidation of **1** by X_2 (X = H, Br, or I) affords pale yellow, diamagnetic 1:1 adducts and is accompanied by appearance of an absorption band in the range 320–385 nm which by comparison with related systems[14] is consistent with formulation of these products as iridium(II) dimers $[(PPh_3)(CO)Ir(X)(\mu\text{-pz})]_2$ incorporating an Ir–Ir bond. This conclusion is substantiated by crystallographic identification[15] of the product **2** from the corresponding reaction with Cl_2 in which (Figure 2) substitution of the 4-position in each pyrazolyl group also occurs, emphasizing the chemical stability of the dimeric system. Occupation of each apical metal site by Cl in a structure which is also dissymmetric (C_2) is accompanied by a marked reduction in the distance between the Ir atoms to 2.737 (1) Å, into the range expected for an Ir–Ir single bond.[16] Complex **2** thus provides the first definitive evidence[17] for the ability of the pyrazolyl group to function as a bridge across a metal–metal bond. Reaction of compound **1** with MeI likewise affords a bright yellow, 1:1 complex, formulated as asymmetric $[(PPh_3)(CO)Ir(Me)\text{-}(\mu\text{-pz})_2\text{-}Ir(I)(CO)(PPh_3)]$ (**3**) on the basis of NMR data.[18] Analogously, reaction of **1** with optically pure 2-methylbutyl iodide affords a related complex (**4**) for which doubling in each of the two distinct ^{31}P NMR shifts is evident. We attribute this to diastereoisomerism in the product, again a consequence of a dissymmetric dimeric structure.

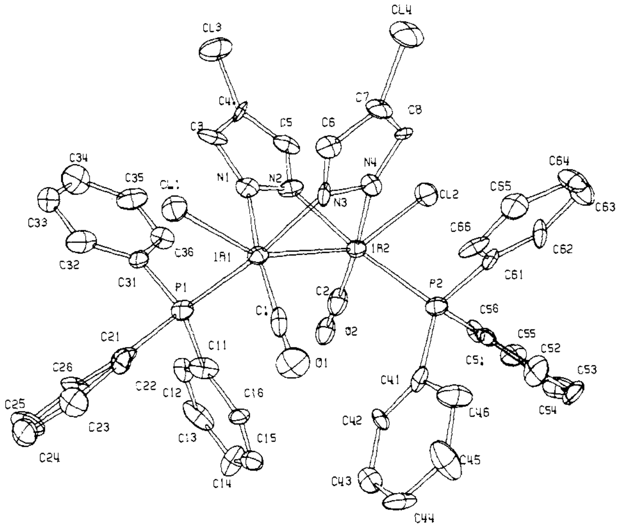

Figure 2. Molecular structure of $[Ir(CO)(PPh_3)(Cl)(\mu\text{-4-Cl-pz})]_2$ (**2**). Atomic labeling has been minimized for clarity but the full scheme is available in the supplementary material. Full details of this structure and that of complex **1** will appear subsequently.

Complexation of small molecules including halogens and alkyl halides to mononuclear metal sites was characterized kinetically[19] as early as 1966 and is particularly well established in the case of Ir(I). By contrast, fragmentation of an alkyl halide in a two-center oxidative addition has remained exceedingly uncommon since it was first identified by Gray et al. at adjacent rhodium atoms in a bridged dimeric cation;[20] the topicality of such addition has been emphasized at some length only recently by Herrmann.[21]

---

(7) Stobart, S. R.; Dixon, K. R.; Eadie, D. T.; Atwood, J. L.; Zaworotko, M. J., first communicated in preliminary form at the XXI International Conference on Coordination Chemistry, Toulouse, France, July, 1980.

(8) Sappa, E.; Tiripicchio, A.; Tiripicchio. Camellini, M. *J. Organomet. Chem.* **1980**, *199*, 243.

(9) In this context we have observed moderately efficient homogeneous hydrogenation in benzene solution of phenylacetylene to styrene and ethylbenzene in the presence of catalytic amounts of complex **1**.

(10) In fact, in a related complex $\{Ir(COD)[\mu\text{-}C_3N_2H(CF_3)(CH_3)]\}_2$ (bridging 3-methyl-5-(trifluoromethyl)pyrazolyl) the Ir_2 separation is yet shorter at 3.07 Å; details of this structure, solved by K. A. Beveridge and G. W. Bushnell will be reported in full subsequently. Very recently endo bidentate (η^2-nonbridging) coordination at a single metal center by the pyrazolyl anion has been identified crystallographically: Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1981**, *20*, 1553.

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

(12) Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940.

(13) Uson, R.; Ciriano, M. A.; Pinillos, M. T.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1981**, *205*, 247.

(14) Mann, K. R.; Gray, H. B. "Inorganic Compounds with Unusual Properties"; *Adv. Chem. Ser.* **1979**, *No. 173*, 225. Maisonnat, A.; Poilblanc, R. *J. Organomet. Chem.* **1978**, *No. 160*, 307.

(15) Crystal data for **2**: $C_{44}H_{37}Cl_4Ir_2N_4O_2P_2$ (bis-CH_2Cl_2 solvate); M = 1314.8; monoclinic; space group $P2_1/n$; a = 15.850 (3), b = 28.616 (4), c = 11.092 (1) Å; β = 95.82 (2)°; Z = 4; Mo Kα radiation, λ = 0.71069 Å; Picker four-circle diffractometer; R = 0.07 for 3748 independent reflections with $F_0^2 > 1\sigma(F_0^2)$. The two CH_2Cl_2 solvate molecules located have been omitted from Figure 2.

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

(17) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 3119. Nesmeyomov, A. N.; Babin, V. N.; Kochetkova, N. S.; Nekrasov, Y. S.; Belousov, Y. A.; Sil'vestrova, S. Y. *Dokl. Chem. Proc. Acad. Sci. U.S.S.R., Chem. Sec.* **1974**, 738.

(18) The ^{31}P NMR spectrum for compound **3** shows two shifts, the close spacing of which (−140.5, −141.8 ppm) is consistent with nonequivalent phosphine ligands each bonded to an iridium(II) center.

(19) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

(20) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461.

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 the research. We are also grateful to Johnson Matthey Inc. for a generous supply of chemicals (S.R.S.).

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.

---

(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

A. W. (Tony) Coleman, Donald T. Eadie, and
Stephen R. Stobart*

Department of Chemistry, University of Victoria
British Columbia, Canada V8W 2Y2

Michael J. Zaworotko and Jerry L. Atwood

Department of Chemistry, University of Alabama
University, Alabama 35486

Received June 22, 1981

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.

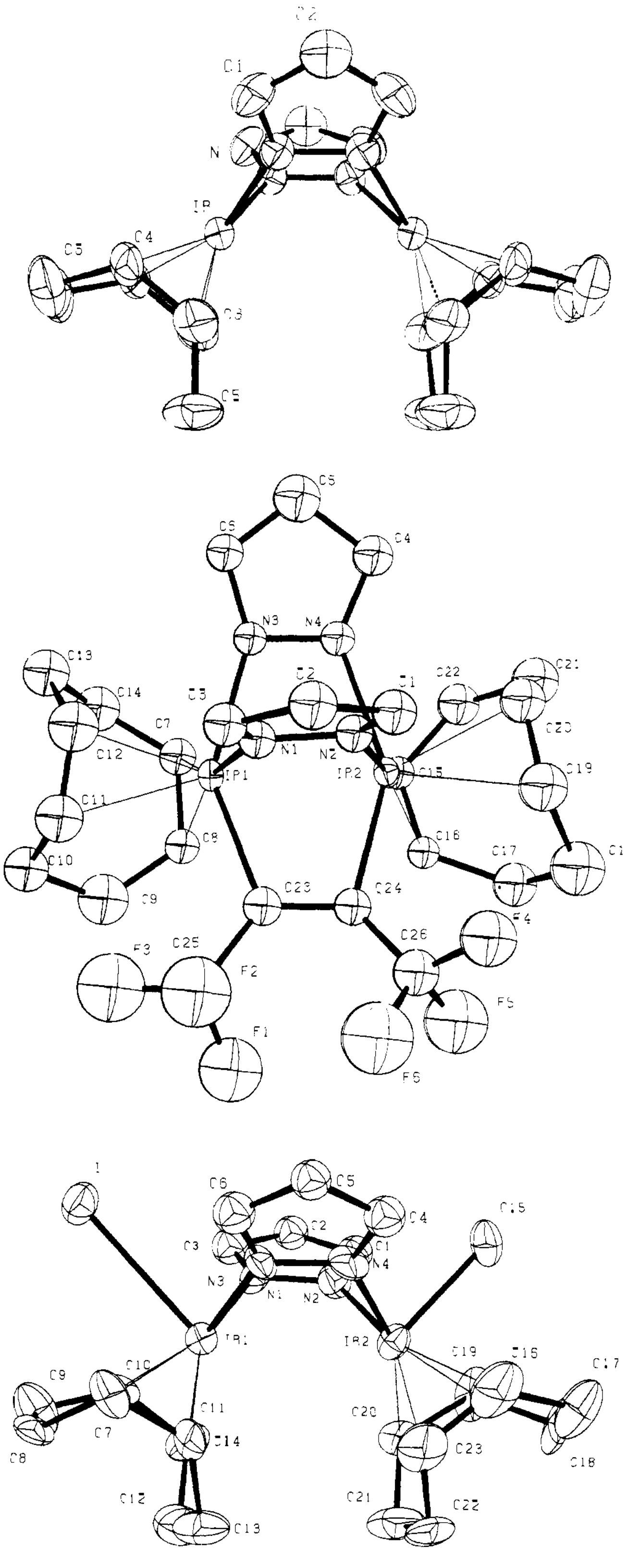

Figure 1. Molecular structures of bis(cyclooctadiene)di-μ-pyrazolyl-diiridium (a) and its adducts with hexafluorobut-2-yne (b) and methyl iodide (c).

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

---

(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