

**Figure 2.** 95-MHz  $^{23}\text{Na}$  Fourier transform NMR spectra of  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{SO}_4$ . (A)  $\text{Na}_2\text{MoO}_4$ , static and spinning at 4.7 kHz and  $\theta = 38^\circ$ ; (B)  $\text{Na}_2\text{SO}_4$ , static and spinning at  $\theta = 48^\circ$  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  $^{23}\text{Na}_2\text{MoO}_4$  and  $^{23}\text{Na}_2\text{SO}_4$  at 8.5 T (corresponding to a  $^{23}\text{Na}$  resonance frequency of 95.2 MHz) for spinning speeds up to  $\sim 6$  kHz. For the static samples, the line widths are reduced to  $\approx 10$ –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 ( $\geq 3$  kHz) rotation well-resolved center bands are obtained (Figure 2A,B) for both  $\text{Na}_2\text{MoO}_4$  ( $\eta = 0$ ) spinning at  $\theta = 38^\circ$  and for  $\text{Na}_2\text{SO}_4$  ( $\eta = 0.6$ ) spinning at  $\theta = 48^\circ$ , 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  $\sim 1$ –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.,  $^{11}\text{B}$ ,  $^{27}\text{Al}$ ,  $^{51}\text{V}$ ,  $^{55}\text{Mn}$ , and  $^{93}\text{Nb}$ ),<sup>12,18</sup> including the observation of fine structure in one system having  $e^2qQ/h = 19.5$  MHz,<sup>12</sup> together with recent independent work on  $^{27}\text{Al}$  by Muller et al.<sup>19</sup> and on  $^{23}\text{Na}$  by Kundla et al.<sup>20</sup> 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 ( $\geq 12$  T) together with the need for development of ultra-high-speed variable-angle spinner assemblies; studies of a variety of organometallics ( $^{55}\text{Mn}$ ,  $^{95}\text{Mo}$ ,  $^{99}\text{Ru}$ ), borates and boron hydrides ( $^{11}\text{B}$ ), oxides ( $^{17}\text{O}$ ), supported catalysts and zeolites ( $^{27}\text{Al}$ ), and metalloprotein model systems ( $^{63}\text{Cu}$ ,  $^{67}\text{Zn}$ ) are currently in progress.

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**Registry No.**  $\text{NaCl}$ , 7647-14-5;  $\text{NaBrO}_3$ , 7789-38-0;  $\text{Na}_2\text{MoO}_4$ , 7631-95-0;  $\text{Na}_2\text{SO}_4$ , 15124-09-1.

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

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The chemistry of polynuclear transition-metal compounds has entered a phase of extremely rapid development, as a consequence of progressive rationalization of synthetic strategy 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<sup>1</sup> or electron delocalization between adjacent atoms<sup>2</sup> or chemically in relation to reactivity at (especially multiple) metal-metal bonds<sup>3</sup> and cooperative catalytic action, including efforts to substantiate a "cluster/surface" analogy.<sup>4</sup> 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<sup>5</sup> on the versatility of the  $\eta^2$ -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*- $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{Cl})$  (Vaska's complex) and pyrazolide anion (ambient, THF, 6 h) affords blood-red crystals of dicarbonylbis(triphenylphosphine)di- $\mu$ -pyrazolyl-di-iridium(I) (**1**) (30–60%), characterized by<sup>6</sup> single-crystal X-ray diffraction (Figure 1). The same compound can be synthesized stepwise from  $[(\text{COD})\text{IrCl}]_2$  ( $\text{COD} = 1,5$ -cyclo-

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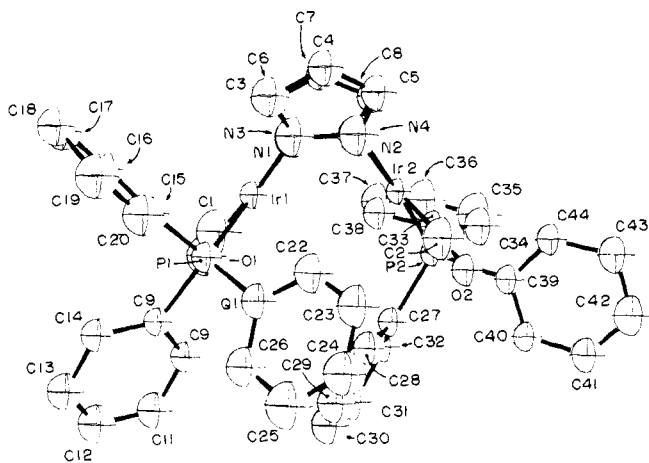
(6) Crystal data for **1**:  $\text{C}_{44}\text{H}_{36}\text{Ir}_2\text{N}_4\text{O}_2\text{P}_2$ ;  $M = 1099.1$ ; triclinic; space group  $P\bar{1}$ ;  $a = 9.992$  (4),  $b = 10.402$  (4),  $c = 20.278$  (8) Å;  $\alpha = 90.01$  (4),  $\beta = 90.10$  (4),  $\gamma = 105.13$  (4)°;  $V = 2037$  Å<sup>3</sup>;  $Z = 2$ ;  $\rho(\text{calcd}) = 1.79$  g cm<sup>-3</sup>; Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å; Nonius CAD4 diffractometer;  $R = 0.046$  for 1481 observed reflections,  $F_o^2 > 3\sigma(F_o^2)$ . 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.

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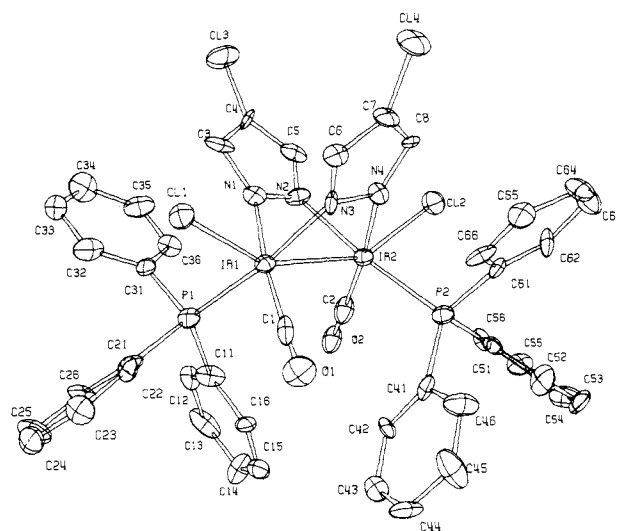


**Figure 1.** Molecular structure of  $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})]_2$  (1). The full atomic labeling scheme is available (with the atomic position and thermal parameters) as supplementary material.

octadiene): treatment with pyrazole/triethylamine affords intensely purple  $[(\text{COD})\text{Ir}(\mu\text{-pz})]_2$  ( $\text{pzH}$  = pyrazole) whence displacement of COD with CO followed by reaction with  $\text{PPh}_3$  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<sup>7</sup> in complex 1 places each pair of ligands (either CO or  $\text{PPh}_3$ ) mutually trans across the metal-metal axis (Figure 1), resulting in a dissymmetric structure belonging to the molecular point-group  $C_2$ . NMR measurements ( $^1\text{H}$  and  $^{31}\text{P}$ ) 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<sup>8</sup> and is of specific interest in relation to asymmetric induction catalysis.<sup>9</sup> 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<sup>5</sup> incorporating exobidentate pyrazolyl bridges<sup>10</sup> and is consistent with some degree of metal-metal interaction as identified by Gray and co-authors in related "face-to-face"  $\text{Rh}(\text{I})$  dimers.<sup>11</sup> Indeed in the structurally similar complex  $[\text{P}(\text{OMe})_3(\text{CO})\text{Ir}(\mu\text{-S-}t\text{-Bu})]_2$  where the Ir centers are linked by single-atom bridges, the separation<sup>12</sup> is actually greater (3.22 Å) while in the rhodium analogue of 1, structurally characterized very recently,<sup>13</sup> the intermetallic distance is very much longer at 3.57 Å.

Oxidation of 1 by  $\text{X}_2$  ( $\text{X} = \text{H}, \text{Br}, \text{or I}$ ) 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



**Figure 2.** Molecular structure of  $[\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Cl})(\mu\text{-4-Cl-pz})]_2$  (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.

with related systems<sup>14</sup> is consistent with formulation of these products as iridium(II) dimers  $[(\text{PPh}_3)(\text{CO})\text{Ir}(\text{X})(\mu\text{-pz})]_2$  incorporating an Ir–Ir bond. This conclusion is substantiated by crystallographic identification<sup>15</sup> of the product 2 from the corresponding reaction with  $\text{Cl}_2$  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.<sup>16</sup> Complex 2 thus provides the first definitive evidence<sup>17</sup> 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  $[(\text{PPh}_3)(\text{CO})\text{Ir}(\text{Me})(\mu\text{-pz})_2\text{-Ir}(\text{I})(\text{CO})(\text{PPh}_3)]$  (3) on the basis of NMR data.<sup>18</sup> Analogously, reaction of 1 with optically pure 2-methylbutyl iodide affords a related complex (4) for which doubling in each of the two distinct  $^{31}\text{P}$  NMR shifts is evident. We attribute this to diastereoisomerism in the product, again a consequence of a dissymmetric dimeric structure.

Complexation of small molecules including halogens and alkyl halides to mononuclear metal sites was characterized kinetically<sup>19</sup> as early as 1966 and is particularly well established in the case of  $\text{Ir}(\text{I})$ . 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;<sup>20</sup> the topicality of such addition has been emphasized at some length only recently by Herrmann.<sup>21</sup>

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**Registry No.** 1, 80461-91-2; 2, 80461-90-1; 3, 80471-11-0; 4, 80462-17-5; [(PPh<sub>3</sub>)(CO)Ir(H)(μ-pz)]<sub>2</sub>, 80462-16-4; [(PPh<sub>3</sub>)(CO)Ir(Br)(μ-pz)]<sub>2</sub>, 80462-15-3; [(PPh<sub>3</sub>)(CO)Ir(I)(μ-pz)]<sub>2</sub>, 80462-14-2; [(COD)Ir(μ-pz)]<sub>2</sub>, 80462-13-1; [(COD)IrCl]<sub>2</sub>, 12112-67-3; *trans*-Ir(PPh<sub>3</sub>)<sub>2</sub>(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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## 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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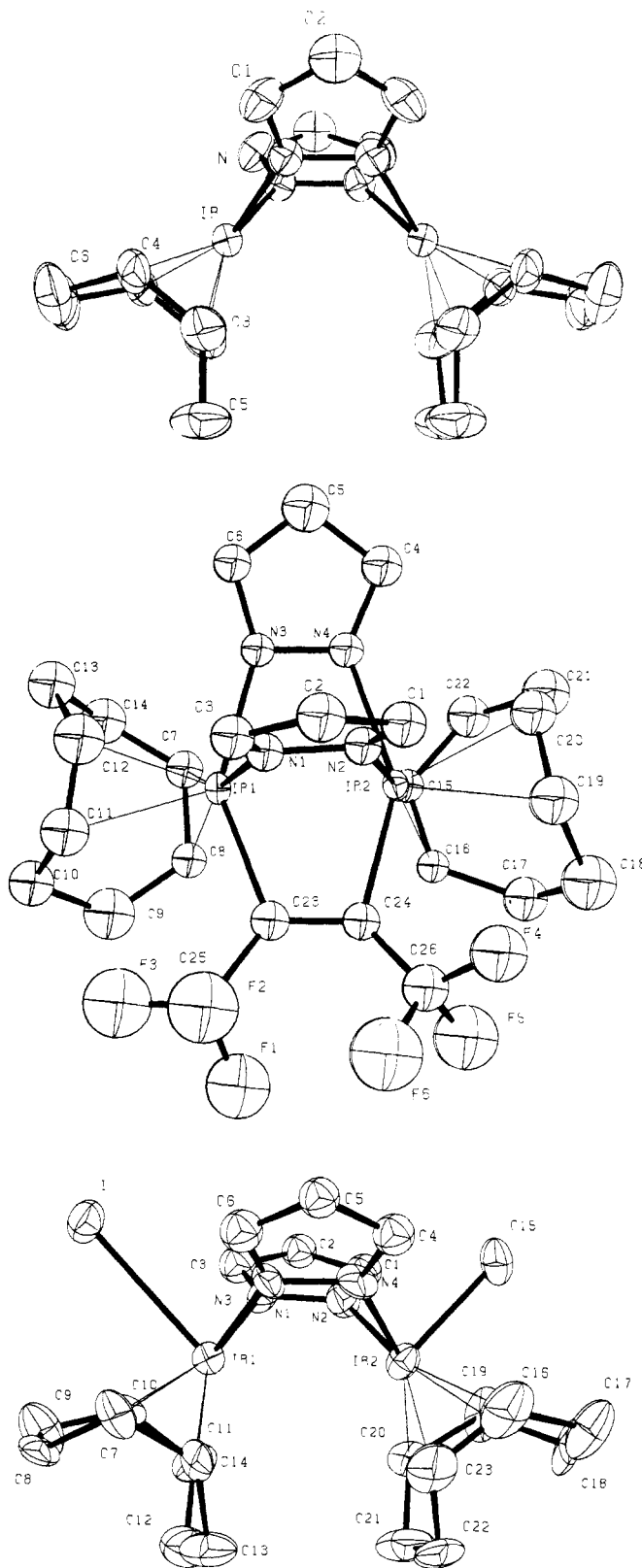
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Transition-metal catalyzed homogeneous reactions frequently depend on sequential oxidative addition/reductive elimination cycles which access two different oxidation states for the metal site. While numerous examples of such behavior occurring at a single coordinately unsaturated metal center exist, only quite recently has attention been focused specifically<sup>1</sup> 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.<sup>2</sup> Pursuing our interest in reactions requiring participation of both metal atoms in a simple dimer compound,<sup>3</sup> 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 trans-

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

formation, i.e., reduction of both metal centers, can be brought about, again without disruption of the dimer.

The structure of the bis(cyclooctadiene)-di-μ-pyrazolyl-diiridium dimer<sup>4</sup> (1), isolated as deep purple crystals from the reaction of [(COD)IrCl]<sub>2</sub> with pyrazole/triethylamine,<sup>3</sup> is represented in Figure 1a. The geometry of the molecule resembles that of the