Mobile Metal–Metal Bonds: Studies on Mixed Valence Ir₃ and Ir₄ Clusters

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Abstract: The dicationic clusters \([\text{CsMe}_5\text{Ir}_2\text{S}_4]^{2+}\) \([(\text{I})^{2+}\) and \([\text{CsMe}_5\text{Ir}_2\text{S}_4]^{2+}\) \[(\text{II})^{2+}\) were prepared by treatment of \([\text{CsMe}_5\text{IrCl}_2]_2\) with \((\text{Me}_3\text{Si})_2\text{S}\) followed by ion exchange chromatography. Crystallographic characterization of the tetrairidium cluster \[(\text{I})^{2+}\) reveals a cubane motif consisting of interpenetrated \text{Ir} and \text{S} tetrahedra. The \text{Ir} core is distorted from idealized tetrahedral symmetry by virtue of a single \text{Ir}–\text{Ir} bonding contact of 2.764(1) Å. The four \text{Ir}–\text{Ir} contacts are nearly equivalent at 3.5 Å, while the \text{Ir}–\text{Ir} distance is 3.683(1) Å. Variable-temperature \(^1\text{H}\) NMR studies indicate that \[(\text{I})^{2+}\) is fluxional with a coalescence temperature of 13 °C (400 MHz), corresponding to \(\Delta G^\circ = 57 \text{ kJ/mol}\). This dynamic process is attributed to migration of the metal–metal bond arising from internal \text{Ir}–\text{Ir} self-exchange. Cyclic voltammetry studies of \[(\text{I})^{2+}\) reveal a pair of reversible one-electron reductions at \(-218\) and \(-487\) mV vs Ag/AgCl. Chemical reduction of \[(\text{I})^{2+}\) was effected with cobaltocene while the neutral cluster could be reoxidized with HCl/O₂. In the solid state \[(\text{II})^{2+}\) features a trigonal-bipyramidal \text{Ir}_2\text{S}_2 core with average \text{Ir–Ir} contacts of 2.82 Å and \text{Ir–S} distances of 2.28 Å. Cyclic voltammetry studies indicate that this close dication undergoes two single electron reductions at \(-712\) and \(-993\) mV. Cobaltocene reduction of \[(\text{II})^{2+}\) afforded dark blue crystals of neutral \[(\text{II})\). Variable-temperature \(^1\text{H}\) NMR spectra of \[(\text{II})\) reveal dynamic behavior, with coalescence at 60 °C (400 MHz), corresponding to \(\Delta G^\circ = 64 \text{ kJ/mol}\). These structural dynamics suggest migration of the nonbonding \text{Ir–Ir} interaction among the three edges of the \text{Ir}_3 triangle.

Introduction

The dynamics of chemical bonds represent a particularly fundamental process. Cases where these dynamics are degenerate and intramolecular are particularly instructive. A molecule which illustrates this phenomenon is bullvalene where all ten carbon centers equilibrate readily at room temperature, eq 1.\(^(*)\) Corresponding examples of skeletal rearrangements involving metal–metal bonds were not known when we began this work. Of course many compounds, metal-containing and otherwise, exhibit dynamic structures (fluxionality), but these dynamics are almost always coupled to or driven by changes in ligation or electron count.\(^(2-3)\) Our interests focus on the mobility of metal–metal bonds in the absence of other changes in the coordination environment about the metals. The degenerate bond/no-bond interchange within a cluster framework is the specific phenomenon of interest.

The cubane clusters \((\text{Ir}_3\text{S}_4)_2\) are especially appealing subjects for the study of the dynamics of metal–metal bonds. Clusters of this category have been prepared for many metals and many main group vertices (E).\(^(4)\) Furthermore, many of these species exist in multiple oxidation states. Important for our studies is the fact that this series of clusters displays systematic structural changes which correlate to cluster electron count. Specifically, the number of metal–metal bonds in the \((\text{Ir}_3\text{S}_4)_2\) clusters corresponds well, but not perfectly,\(^(5)\) with cluster electron count.

Figure 1. Idealized structures of \((\text{Ir}_3\text{S}_4)_2\) and \((\text{Ir}_3\text{S}_4)_2\) cluster cores showing patterns of localized M–M bonding as a function of electron count.

The number of metal–metal bonds in the \((\text{CsMe}_5\text{Ir}_3\text{S}_4)_2\) clusters corresponds well, but not perfectly,\(^(5)\) with cluster electron count. In general, the intermetallic distances increase as the cluster electron count increases from 60 to 72. The fact that this trend is the reverse of that seen for metal radii is strong evidence for the dominant role of metal–metal interactions. For the sulfido cubane clusters the electron counts represent the sum of 24 e⁻ from the four \text{S}²⁻ vertices and 36 e⁻ from the four \text{C₄Ir}₃⁻ ligands, in addition to the valence d electrons associated with the four trivalent metals. The metal–metal bond order for the members of this series ranges from six for the 60 e⁻ \text{Mo}_4 clusters to zero for 72 e⁻ \text{Co}_4 species,\(^(6)\) see Figure 1. This trend indicates that the acceptor orbitals in these >60 e⁻ clusters are metal–metal antibonding. Clusters with electron counts intermediate between 60 and 72 are expected to exhibit net metal–metal bond


\(^{3}\) The exception to this pattern is the dynamic interchange of long and short W–W bonding interactions in \((\text{W}(\text{O}-\text{Pr})_2)_2\) Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. J. Am. Chem. Soc. 1989, 11(1), 574.

\(^{4}\) Harris, S. \\textit{Polyhedron} 1988, 8, 2843.


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Figure 2. Cyclic voltammograms of CH$_2$Cl$_2$ solutions of [(C$_5$Me$_5$)$_4$Ir$_2$]PF$_6$ (A) and [(C$_5$Me$_5$)$_3$Ir$_2$S$_2$]PF$_6$ (B) referenced to Ag/AgCl, with a scan rate of 100 mV/s.

orders intermediate between six and zero. The cluster (RC$_5$H$_4$)$_3$Fe$_4$S$_4$ follows this pattern with two short (bonding) Fe-Fe contacts of 2.6 Å.° The similar patterns are seen in other low-spin Fe-S and Fe-Se clusters.°

The structures of the (C$_5$R$_5$)$_2$Ru$_3$ clusters correlate with their electron counts as determined by Wade's rules.° Those with 48 e$^-$ typically exhibit three metal-metal bonds while those with 54 e$^-$ are predicted to contain one metal-metal bond (Figure 1). The energetically subtle distinction between localized and delocalized M-M interactions is illustrated by Otsuka’s 50 e$^-$ clusters of the type (C$_5$R$_5$)$_2$CoS$_2$, which have been extensively studied by the Dahl group.® Such species adopt both D$_3$h and nido structures depending on the substituents on the cyclopentadienyl ligands.°

Our experience indicates that such subtleties are less important for clusters derived from the second- and third-row metals. This point is illustrated by the neutral and dicatonic clusters of the type [(cycmene)$_2$Ru$_2$S$_2$]$^+$, which have been examined by single crystal X-ray diffraction.°° The oxidized (z = 2+) and reduced (z = 0) states adopt spin-paired closo (D$_3$h) and nido (C$_6$h$_5$) structures, respectively. Similar structural trends have been observed for phosphinidene clusters of the type Fe$_2$(PR$_3$)$_2$(CO)$_3$.°°°

Our interests in mobile metal-metal bonds originated with the finding that the 66 e$^-$ cluster [(RC$_5$H$_4$)$_2$Ru$_2$S$_2$]$^+$ adopts a localized structure in the solid state with three Ru–Ru bonding interac-

Results

Synthesis of [(C$_5$Me$_5$)$_4$Ir$_2$S$_4$] and [(C$_5$Me$_5$)$_3$Ir$_2$S$_2$]. Treatment of a methanol/THF slurry of [(C$_5$Me$_5$)IrCl$_2$]$_2$ with (Me$_3$Si)$_2$S produced a mixture of water-soluble products which were separated into green and yellow fractions using ion exchange chromatography. Addition of excess KPF$_6$ to each fraction precipitated CH$_2$Cl$_2$-soluble salts analyzing as [(C$_5$Me$_5$)$_3$Ir$_2$S$_2$]PF$_6$ ([(C$_5$Me$_5$)$_4$Ir$_2$]Cl$_2$) and [(C$_5$Me$_5$)$_3$Ir$_2$S$_2$]PF$_6$ ([(C$_5$Me$_5$)$_4$Ir$_2$]Cl$_2$) in 54 and 4% yields, respectively. These formulations were supported by FAB mass spectrometry, elemental analysis, and X-ray crystallography (see below).

The formation of the Ir$_3$ cluster can be rationalized on the basis of the stoichiometry of the reactants (eq 2). The observation of the mixed valence cluster [I]$_3^+$ suggests that the CH$_3$OH/(Me$_3$Si)$_2$S mixture generates a species capable of oxidizing some of the iridium to the tetravalent state. This oxidation is associated with the methanolysis of (Me$_3$Si)$_2$S, since the reaction of [(C$_5$Me$_5$)IrCl$_2$]$_2$ with (Me$_3$Si)$_2$S in a THF solution affords the (Ir$_3$)$_2^+$ cluster exclusively. The addition of oxidizing equivalents in the form of elemental sulfur to the reaction of [(C$_5$Me$_5$)IrCl$_2$]$_2$ and (Me$_3$Si)$_2$S led to a 5-fold increase in the yield of [I]$_3^+$ (eq 3).

Control experiments showed that [2]$_3^+$ does not convert to [1]$_2^+$ under relevant conditions, for example [2]$_3^+$ does not react with sulfiding agents. Thus, it appears that the [1]$_3^+$/[2]$_3^+$ distribution is established early in the reaction sequence. The added elemental sulfur employed in the synthesis of [1]$_3^+$ is involved at an intermediate mechanistic stage since neither [1]$_2^+$ nor [(C$_5$Me$_5$)IrCl$_2$]$_3$ is reactive toward S$_8$.

Electrochemistry and Redox Reactions. Cyclic voltammetry of a CH$_2$Cl$_2$ solution of [1]$_2^+$ showed 1 e$^-$ reductions at -218 and -487 mV vs Ag/AgCl (Figure 2A). Scanning to still more positive potentials revealed a possible oxidation to [I]$_3^+$ at 930 mV. On the basis of the two E$_{1/2}$’s the conproportionation constant for the formation of [1]$_2^+$ from [1]$_3^+$ was calculated to be 90. The i$_S$/i$_C$ ratios of 0.795 to 0.877 for the two waves suggest electrochemical reversibility (total reversibility at an electrode).

Plots of the square root of the scan rate vs peak current were linear over nine scan rates ranging from 25 to 500 mV indicating that the redox events are diffusion controlled and are not subject to rate limiting structural changes. As suggested by the electrochemical results, solutions of [1]$_2^+$ underwent reduction by 2 equiv of (C$_5$H$_5$)$_2$Co affording good yields of neutral [(C$_5$Me$_5$)$_3$Ir$_2$S$_2$] (eq 4).


(8) In contrast to more recent work on Fe–Se clusters, the crystallographic analysis of [(RC$_5$H$_4$)$_2$Fe$_2$S$_2$]$^+$ indicates a partially delocalized structure. Four Fe–Fe contacts of intermediate length (2.8 Å) are observed which Dahl et al. assign to a bond order of 3/4.


The $^1$H NMR spectrum of this red species [1] exhibits a single resonance at 1.72 ppm ($\text{C}_5\text{D}_5n$), as reported by Dobbs and Bergman who prepared it from ($\text{C}_5\text{Me}_5$)$_2\text{Ir}_4(\mu_2\text{S})(\text{PF}_6)_2$. The neutral tetrairidium cluster was cleanly oxidized by HCl in air to give $[1]^{2+}$. While the optical spectrum of neutral [1] is featureless at wavelengths above 338 nm, solutions of [1]$^{2+}$ are green as indicated by a rather strong absorption at 636 nm, $\log \epsilon = 1.99$ (Figure 3).

Cyclic voltammetric studies on $\text{CH}_2\text{Cl}_2$ solutions of $[2]^{2+}$ revealed 1 $e^-$ reductions at $-712$ and $-993$ mV (Figure 2B). Measurements out to 1.5 V failed to show evidence for further oxidation to the Ir$^{IV}$ level. The $i_s/i_c$ ratios of 0.911 to 0.920 for the two waves indicate electrochemical reversibility. The dependence of the square root of the scan rate vs the peak current over scan rates ranging from 25 to 500 mV was found to be linear. The conproportionation constant for the formation of $[2]^{2+}$ from $[2]^{2+}$ and $[2]^{0}$ is 117. Reduction of $[2]^{2+}$ using 2 equiv of ($\text{C}_5\text{H}_5$)$_2$Co gave the extremely air sensitive neutral derivative [(C$_{5}$H$_{5}$)Ir$_{4}$S$_{4}$].

The deep blue color of this mixed valence cluster results from a strong absorbance at 592 nm ($\log \epsilon = 2.28$), in contrast to the pale yellow color of $[2]^{2+}$ ($\lambda_{max} = 344$ nm) (Figure 4). Results of the electrochemical studies are presented in Table 1.

**NMR Studies of ($\text{C}_5\text{Me}_5$)$_2\text{Ir}_4\text{S}_4^{2+}$.** The $^1$H NMR spectrum of $[1]^{0}$ consists of a singlet at 1.72 ppm. It appears that the four Ir centers are equivalent as confirmed by the crystal structure analysis described by Bergman and Dobbs. In contrast, the room temperature $^1$H NMR spectrum of $[1]^{2+}$ suggested dynamic behavior since it consisted of a very broad singlet (Figure 5). Essentially the same spectrum is observed for aqueous solutions of $[1]Cl_2$ and for $\text{CD}_2\text{CN}$ and $\text{CD}_2\text{Cl}_2$ solutions of $[1](\text{PF}_6)_2$. Variable-temperature measurements revealed that the broad singlet sharpened at higher temperatures and split into two sharp singlets at low temperatures. At 400 MHz the coalescence temperature was $13 \pm 3^\circ$C corresponding to $\Delta H^* = 57$ kJ/mol, according to the Gutowsky–Holm relationship. The NMR spectra were digitally simulated over a range of temperature from $-37$ to $38 \pm 3^\circ$C. There is a slight temperature dependence of the chemical shifts in the experimental spectra, however, the chemical shift difference of the two exchanging sites was assumed to be temperature independent for the simulation. The simulations yielded the following activation parameters: $\Delta H^* = 80 \pm 10$ kJ/mol and $\Delta S^* = 82 \pm 36$ J/(mol K). These values give a calculated $\Delta G_{298}^{\circ}$ value of $56 \pm 15$ kJ/mol, which is in agreement with the calculation from the coalescence temperature. The $^{13}$C-$^1$H NMR spectrum at $-50^\circ$C showed two pairs of resonances corresponding to two sets of nonequivalent $\text{C}_5\text{Me}_5$ groups (Figure 6A). The exchange rates for [(C$_5$Me$_5$)$_2$Ir$_4$S$_4$]$^{2+}$ were found to be independent of concentration, hence they are associated with an intramolecular process.

Methylated ligands are particularly well suited for $^{13}$C NMR analysis in the solid state by CP-MAS techniques. The spectrum of a solid sample of [(C$_5$Me$_5$)$_2$Ir$_4$S$_4$]($\text{PF}_6$)$_2$ was examined to demonstrate the rigidity of the metal–metal bond in the solid state. In the methyl region, the resonances at 9.99 and 9.25 ppm were assigned to the two sets of nonequivalent C$_5$Me$_5$ groups, while in the aromatic region a signal at 95.68 and a pair of signals at 105.23 and 106.89 ppm were observed. The pair of closely spaced high frequency signals are assigned to the (C$_5$Me$_5$)Ir sites which are slightly nonequivalent due to the low crystallographic site symmetry (Figure 6B). For comparison, the solid-state CP-MAS spectrum of $[1]^{2+}$ has a singlet at 8.98 for the methyl carbons and a singlet at 88.98 ppm for the aromatic carbons, corresponding to equivalent C$_5$Me$_5$ groups. These measurements suggest that the low-field C$_5$Me$_5$ signal at 95.68 ppm in the spectrum of $[1]^{2+}$ is associated with Ir$^{III}$ sites.

**NMR Studies of [(C$_5$Me$_5$)$_2$Ir$_4$S$_4$]$^{2+}$.** The 400-MHz $^1$H NMR spectrum of a CD$_2$CN solution of $[2]^{2+}$ consists of a sharp singlet

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**Table 1. Electrochemical Data for $[1]^{0}$ and $[2]^{2+}$ at Scan Rates of 100 mV s$^{-1}$.**

<table>
<thead>
<tr>
<th>compd</th>
<th>$E_{pa}(1)^{a}$ (mV)</th>
<th>$E_{pa}(1)^{a}$ (mV)</th>
<th>$i_s/i_c$</th>
<th>$E_{pa}(2)^{a}$ (mV)</th>
<th>$E_{pa}(2)^{a}$ (mV)</th>
<th>$i_s/i_c$</th>
</tr>
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<tr>
<td>[(C$_5$Me$_5$)$_2$Ir$_4$S$_4$]$^{2+}$</td>
<td>-252</td>
<td>-317</td>
<td>0.80</td>
<td>-515</td>
<td>-587</td>
<td>0.88</td>
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<tr>
<td>[(C$_5$Me$_5$)$_2$Ir$_4$S$_4$]$^{2+}$</td>
<td>-679</td>
<td>-745</td>
<td>0.91</td>
<td>-957</td>
<td>-1029</td>
<td>0.93</td>
</tr>
</tbody>
</table>

$^{a}$ $E_{pa}(1)$ and $E_{pa}(2)$ refer to the peak potentials of the anodic and cathodic waves, respectively.
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Figure 5. Experimental and simulated variable-temperature 400-MHz $^1$H NMR spectra of [(C$_5$Me$_5$)$_3$IrS$_4$](PF$_6$)$_2$ (CD$_2$Cl$_2$ solution).

Figure 6. Experimental and simulated variable-temperature 400-MHz $^1$H NMR spectra of [(C$_5$Me$_5$)$_3$IrS$_4$] (C$_6$D$_6$CD$_3$ solution). The singlet at ~2 ppm is due to an impurity.

Figure 7. $^{13}$C ([$^1$H]) 100-MHz NMR spectrum of a CD$_2$Cl$_2$ solution of [(C$_5$Me$_5$)$_3$IrS$_4$](PF$_6$)$_2$ (-50 °C) (A). $^{12}$C($^1$H) CP-MAS 75.5-MHz NMR spectrum of microcrystalline [(C$_5$Me$_5$)$_3$IrS$_4$](PF$_6$)$_2$ (B).

Crystallographic Studies on [(C$_5$Me$_5$)$_3$IrS$_4$](PF$_6$)$_2$. The salt features a distorted cuboidal (C$_5$Me$_5$)$_3$IrS$_4$ cluster with well-separated PF$_6^-$ counterions, as well as two molecules of acetone. Crystallographic symmetry was not imposed on the cations. Of interest are the nature and the degree of the deviations of the Ir$_4$ core from tetrahedral symmetry (Figure 8, Table 2). The cluster is distorted by virtue of the short Ir(2)–Ir(3) contact of 2.764(1) Å resulting in a Ir$_4$ core of idealized C$_2$ symmetry. These two iridium centers are assigned to the Ir$^{IV}$ oxidation state and the short distance is interpreted as a direct metal-metal bond. For comparison the Ir–Ir bonding distance in iridium metal is 2.71 Å,$^{17}$ while the still more appropriate structural model Ir$_4$(CO)$_{12}$ has Ir–Ir contacts of 2.69 Å.$^{18}$ The four Ir$^{III}$–Ir$^{IV}$ contacts (3.563(1)–3.586(1) Å) are assigned as nonbonding. For comparison the six Ir–Ir contacts in the parent 72 e– cluster (C$_7$R$_5$)$_3$Ir$_4$S$_4$ fall in the narrow range of 3.584–3.602 Å. The unique Ir$^{III}$–Ir$^{III}$ interaction in [1]$^{2+}$ has the longest contact of 3.683(1) Å. The

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Figure 8. ORTEP drawing of the dication in [(CsMe)IrS2](PF6)2 with the non-hydrogen atoms removed for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [(CsMe)IrS2](PF6)2 ([2]+)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1–Ir2</td>
<td>3.565(1)</td>
</tr>
<tr>
<td>Ir1–Ir4</td>
<td>3.683(1)</td>
</tr>
<tr>
<td>Ir2–Ir4</td>
<td>3.563(1)</td>
</tr>
<tr>
<td>S1–S2</td>
<td>3.632(7)</td>
</tr>
<tr>
<td>S1–S3</td>
<td>3.079(7)</td>
</tr>
<tr>
<td>S2–S4</td>
<td>3.063(7)</td>
</tr>
<tr>
<td>Ir2–S1</td>
<td>2.325(5)</td>
</tr>
<tr>
<td>Ir2–S2</td>
<td>2.329(5)</td>
</tr>
<tr>
<td>Ir1–S1</td>
<td>2.413(5)</td>
</tr>
<tr>
<td>Ir4–S3</td>
<td>2.385(5)</td>
</tr>
<tr>
<td>Ir2–S4</td>
<td>2.378(5)</td>
</tr>
<tr>
<td>S1–Ir1–S2</td>
<td>80.2(2)–103.1(2)</td>
</tr>
<tr>
<td>S1–Ir1–Ir2</td>
<td>77.1(2)–81.7(2)</td>
</tr>
<tr>
<td>S1–Ir1–Ir3</td>
<td>73.1(2)–73.3(1)</td>
</tr>
</tbody>
</table>

Bonding IrIII–S (2.308(5)–2.413(5) Å) and IrIV–S (2.308(5)–2.384(5) Å) distances are quite similar.

Using molecular modeling techniques we examined the possibility of close H–H contacts in [1]2+. Hydrogen atom positions were calculated on the basis of idealized tetrahedral methyl carbon centers and the methyl groups were rotated so as to bring the H atoms into closest contact. The closest H–H contact is 1.23 Å between methyl groups on two IrIV centers. The van der Waals radius for hydrogen is 1.2 Å. Although these calculations show that these methyl groups can clash sterically, they overstate any problems since other methyl rotamers show H–H contacts beyond the van der Waals range.

Crystallographic Studies on [(CsMes)2IrS2](PF6)2. The salt features a roughly trigonal bipyramidal IrS2 core with well-separated PF6− counterions as well as one acetone molecule. Crystallographic symmetry was not imposed on the cation (Figure 10, Table 3). The three Ir–Ir bonds are nearly equivalent (2.8201(7)–2.8157(7) Å) as are the Ir–S distances (2.275(3)–2.294(3) Å). The degree of pyramidalization at sulfur is indicated by the Ir–S–Ir angles (76.0°–76.46°) which are larger than those of the cobalt analog [(C5H4Me)2Co(S2)2]2+(SbF6)2 with Co–S–Co angles of 71.6° to 74°. A space-filling diagram demonstrates the decreased crowding in the IrS2 molecule, with closest H–H contacts of 1.98 Å between CsMes groups and 1.66 Å between H atoms within a given CsMes ligand (Figure 11).

Discussion

This project was developed to prepare and examine clusters exhibiting mobile metal–metal bonds. Our efforts were rewarded by a one-pot route to two types of clusters which exhibit this property. Specifically, [(CsMe)IrCl2]2 was found to react with a mixture of (Me3Si)2S and elemental sulfur to give both [(CsMes)3Ir3S4]2+ and [(CsMes)Ir4S4]2+. We propose that the two clusters arise via the initial formation of (CsMes)2Ir2(p2-S)2. This same species has been invoked previously in the thermal condensation of (CsMes)2Ir2(p2-S)2(PMe3) to give (CsMes)4Ir4S4 with loss of phosphine. Conceivably the Ir3S2 cluster arises by the complexation of (CsMes)2Ir2(p2-S)2 with (CsMes)IrCl2 followed by loss of chloride. The formation for the mixed valence cubane cluster is not as easily explained, although our control
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experiments suggest that it is an intermediate not the starting or final product which reacts with the added sulfur. It seems likely that \((\text{C}_2\text{Me}_5)_2\text{Ir}_2(\mu_2\text{S})_2\) would be reactive toward sulfur to give persulfido species.\(^{15}\)

As seen for many other cyclopentadienyl metal sulfide clusters, both \([1]^2\) and \([2]^0\) undergo redox reactions under conditions that are electrochemically addressable. The results of cyclic voltammetry experiments guided the selection of redox agents employed to generate the mixed valence clusters. Within the context of mononuclear chemistry there is no simple explanation for the nature of the redox processes observed. In one case, the low potential processes interrelate \(\text{Ir}^{III}\) and \(\text{Ir}^{IV}\) states while in the effect of the two redox steps is the making or breaking of \(\text{Ir}^{II}\)–\(\text{Ir}^{III}\) nature of the redox processes observed. In one case, the low visible spectrum of the neutral homovalent cluster.

In the visible region. The solid-state structure of this species cuboidal cluster with only one \(\text{M}–\text{M}\) bond. It represents a new that allow the degenerate hopping of the bond or nonbond. The reversible formation/destruction of metal–metal bonds in bimetallic complexes is well-known when the two metals are constrained by a ligand bridge.\(^{20}\) The unusual aspect of \([1]^2+\) and \([2]^0\) is that the metal–metal bonds are situated in frameworks that allow the deprotonating hopping of the bond or nonbond. The species \([(\text{C}_5\text{R}_5)_2\text{Ir}_2\text{S}_2]^2+\) is an unusual example of a cuboidal cluster with only one \(\text{M}–\text{M}\) bond. It represents a new among the series of clusters presented in Figure 1. Within this family of clusters, those with cluster electron counts not divisible by four are necessarily mixed valence and are potentially subject to deprotonation of the metal–metal bond. Indicative of the mixed valence character of \([1]^2+\) is the appearance of a strong low-energy electronic band in contrast to the featureless visible spectrum of the neutral homovalent cluster.

Iridium(IV) compounds are typically associated with electronegative ligands which are capable of ligand-to-metal \(\pi\)-donation, such as \(\text{IrCl}_4^{2-}\).\(^{21}\) \(\text{Ir}^{IV}\) is also known to be stabilized by \(\text{IrC}_16^{2-}\).\(^{21}\) \(\text{Ir}^{IV}\) is also known to be stabilized by trinegativeligands which are capable of ligand-to-metal \(\text{S}–\text{d}\)-donation, such as \(\text{IrS}_6^{2-}\).\(^{21}\) A highly symmetric structure of this diamagnetic species suggests a delocalized ground state.\(^{25}\) It is very likely that \(\text{N}–\text{Ir}\) \(\pi\)-bonding plays a significant role in the stabilization of this species, especially since the \(\text{Ir}–\text{Ir}\) separations are beyond bonding distances.

The trimetallic cluster \([(\text{C}_2\text{Me}_5)_2\text{Ir}_2\text{S}^2]^2+\) is a highly symmetrical species featuring three \(\text{Ir}–\text{Ir}\) bonding interactions. Reduction of this species to the mixed valence \((\text{Ir}^{III})_2\text{Ir}^{IV}\) cluster is also accompanied by the appearance of a strong absorption band in the visible region. The solid-state structure of this species was not determined; however, it was assumed to be analogous to \([(\text{cymene})_2\text{Ru}_2\text{S}_2]^8+\), which was characterized by single crystal X-ray diffraction.\(^{11}\) This Ru\(_2\)Ru\(_2\) cluster adopts an idealized \(\text{C}_6\) core as seen for all five-vertex, 50 e–clusters.\(^{12}\) The present results suggest that this Ru\(_2\) cluster may also exhibit dynamics associated with mobile Ru–Ru bonds.


Figure 11. Space filling diagram of the dication in \([(\text{C}_2\text{Me}_5)_2\text{Ir}_2\text{S}^2](\text{PF}_6)^2-\). Hydrogen positions were calculated. The following van der Waals radii (Å) were used for this drawing: C, 1.60; H, 1.20; Ir, 2.30; S, 1.85. The Ir atoms are stipled.

The DNMR studies demonstrate the mobility of the metal–metal bonds in \([1]^2+\) and \([2]^0\). The DNMR patterns are consistent with the movement of one bond or one nonbond as in the case of \([2]^0\). The rates are first order and the dynamics are intramolecular since the barriers are independent of concentration. CP-MAS measurements on \([1](\text{PF}_6)^2\) indicate that the cluster core is rigid in the solid state. This is expected since the crystallographic studies show that the single \(\text{Ir}–\text{Ir}\) bond is associated with a substantial distortion of the \(\text{Ir}_4\) core from tetrahedral symmetry. Thus the shift of the \(\text{Ir}–\text{Ir}\) bond entails the elongation of one bond by 0.9 Å and the contraction of one bond by the same amount, as well as 0.1 Å changes associated with the shift of the \(\text{Ir}^{III}–\text{Ir}^{III}\) contact. Such motion is not expected to occur in a solid where many of the atomic positions are constrained by electrostatic and van der Waals forces.

The mechanism by which the \(\text{Ir}–\text{Ir}\) bonds and nonbonds migrate among the equivalent sites has not been established. The disparate values of the entropies of activation (±82 ± 36 J/(mol K) for \([1]^2+\) and \(-72 ± 15 J/(mol K) for \([2]^0\)) for the dynamics of \([1]^2+\) and \([2]^0\) are difficult to explain. In the case of \([1]^2+\), the stepwise relocation of the \(\text{Ir}–\text{Ir}\) (non)bonding interaction to an adjacent edge can be effected via electron transfer from one of two \(\text{Ir}^{III}\) centers to one of two \(\text{Ir}^{IV}\) sites (eq 6).

These aforementioned mechanisms are simplified in that they focus exclusively on the metal–metal bonds. Furthermore our
description relies on assignments of formal oxidation states. An alternative description of these dynamics can be developed on the basis of molecular orbital theory. For example, Fenske and co-workers have discussed the relationship between the electron counts and geometry of organometallic $\text{M}_n\text{S}_2$ clusters. The basis of molecular orbital calculations the $D_{3h}$ core structures of 48 e$^-$ clusters like [2]$^{2+}$ can be rationalized, with the HOMO consisting of nonbonding t$_{2g}$-like orbitals centered on the metals. For the corresponding 50 e$^-$ clusters such as [2]$^0$, the two added electrons would occupy orbitals that transform as e' and a'. This configuration would be subject to a Jahn-Teller distortion to give a cluster with $C_{3v}$ symmetry. Under this reduced symmetry, the HOMO then transforms as $b_2$ and is doubly occupied. If one accepts this model, then the barrier controlling the dynamics in [2]$^0$ is a measure of the stabilization resulting from the Jahn-Teller distortion.

The present work provides particularly simple examples of mobile metal-metal bonds in cluster frameworks. There are still only a few examples of this phenomenon, and the factors that control the energetics are not well understood. Experiments designed to probe the mechanism of the dynamics are underway.

**Experimental Section**

**Materials.** The hydrated trichloride of iridium was obtained from Johnson Matthey. [(C$_5$Me$_5$)IrCl$_3$]$^{28}$ and (Me$_3$Si)$_2$S (Caution: STENCH!)$^{29}$ were prepared according to literature methods. (C$_5$H$_5$)$_2$Co (Aldrich) was vacuum sublimed at 40 °C. Tetrahydrofuran, benzene, and hexanes were distilled from Na/K alloy. Dichloromethane and acetonitrile were distilled from CaH$_2$. Methanol (Fischer) was used as received. All solvents were deoxygenated with dry O$_2$-free nitrogen.

**Methods.** Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Positive ion FAB mass spectra were recorded on a VG ZAB-SE instrument at the SCS Mass Spectrometry Laboratory using the “Magic Bullet” matrix (3:1 mixture of dithioerythritol–dithiothreitol). The results are reported for $^{195}$Ir. Solution $^1$H and $^{13}$C NMR spectra were recorded on a Varian U400 spectrometer while CP-MAS measurements employed a GE WB 300-MHz instrument. UV–vis spectra were measured on a Hewlett Packard 8452A spectrometer using a 1 cm path length quartz cell. The data are reported with $\Delta$H$_{\text{max}}$ in nm (log e in M$^{-1}$ cm$^{-1}$). Preparative operations, unless otherwise stated, were performed under an atmosphere of nitrogen using standard Schlenk techniques.

**Electrochemistry.** Electrochemical experiments were carried out on a Bioanalytical Systems BAS-100 electrochemical analyzer. Cyclic voltammograms were measured on $\sim$10$^{-3}$ M CH$_3$Cl$_2$ solutions with 0.1 M n-Bu$_4$NPF$_6$ as the supporting electrolyte and Pt working and counter electrodes vs Ag/AgCl. Under these conditions, the (C$_5$H$_5$)$_2$Fe$^{3+}$/Fe$^{2+}$ couple was +572 mV ($E_{\text{p}}$) and +577 mV ($E_{\text{p}}'$). In the case of [2]$^{2+}$, the HOMO then transforms as $b_2$ and is doubly occupied. If one accepts this model, then the barrier controlling the dynamics in [2]$^0$ is a measure of the stabilization resulting from the Jahn-Teller distortion.

**Dynamic NMR Simulations.** The free energy of activation can be calculated from the coalescence temperature ($T_c$) and $\Delta\nu$, the separation (in Hz) between the two signals via the following equations.$^{31}$

\[ K_s = \exp\left(\frac{E_0 - E_{\text{p}}}{RT}\right) \]

\[ \Delta G_m = 19.14T_c[10.32 + T_c/\Delta\nu] \text{ J/mol} \]

\[ k_s = 2.22k_0 \]

$^{27}$ A further refinement of this model could consider a single $D_{3h}$ transition state (or intermediate) where the configuration of the HOMO is (e')$^2$ or (a')$^2$. $^{28}$ White, C.; Yates, A.; Maillis, P. Inorg. Synth. 1992, 29, 230.


$^{31}$ Morse, P. M.; Spencer, M. H.; Wilson, S. R.; Girolami, G. S. Organometallics 1994, 13, 1646-1655.


$^{33}$ Morse, P. M.; Spencer, M. H.; Wilson, S. R.; Girolami, G. S. Organometallics 1994, 13, 1646-1655.
and 20 mL of CH₃OH was treated with 0.3 mL (1.43 mmol) of (Me₂Si₂)₂S. The reaction mixture was then treated with 0.185 mL (0.942 mmol) of (Me₃Si)₂S. The resulting brown solution was evaporated to dryness. The green-yellow salts which were extracted into 20 mL of benzene were purified as above, resulting in 0.1087 g of [(C₅Mes)Ir₄S₄(PF₆)]₂ (22%) and 0.177 g of [(PF₆)₂] (47% yield).

(b) In methanol—THF with added sulfur: A mixture of 0.469 g (0.589 mmol) of [(C₅Mes)IrCl₂]₂ and 9.4 mg (0.294 mmol) of (CsMes)₄Ir₄S₄ in 10 mL of CH₂Cl₂ was treated with 0.141 mL (0.664 mmol) of (CsMes)I (b) in methanol—THF. After 1.5 h the solution was concentrated to 10 mL and diluted with 50 mL of hexanes to give 0.030 g of [(CsMes)IrCl₂]₂ and 10 mg (0.314 mmol) of [(C₅Mes)Ir₄S₄(PF₆)]₂. The orange reaction mixture was heated under reflux for 48 h. The resulting brown solution was evaporated to dryness. The green-yellow salts which were extracted into 20 mL of H₂O, filtered to remove a brown residue, and loaded onto a 10 × 1 cm column of Sephadex CM-25 cation exchange resin (Na form). Elution with 0.05 M NaCl gave a yellow band followed by a green band. Addition of 2 g (10.0 mmol) of KPF₆ to each of these fractions resulted in the precipitation of 9.4 mg (0.294 mmol) of [(CsMe₅)IrCl₂]₂ and 0.272 g of [(PF₆)₂] (47% yield).

(c) In THF: A slurry of 0.50 g (0.628 mmol) of [(CsMe₅)IrCl₂]₂ in 70 mL of THF and 20 mL of methanol and then treated with 0.185 g (0.589 mmol) of (Me₅Si)₂S. The mixture was refluxed for 48 h, resulting in a brown solution. The crude product was extracted into H₂O and purified as above, resulting in 0.1087 g of [(1)(PF₆)₂] (22%) and 0.177 g of [(2)(PF₆)₂] (47%).

(d) In THF, with added sulfur: A slurry of 0.50 g (0.628 mmol) of [(CsMe₅)IrCl₂]₂ and 10 mg (0.314 mmol) of S₈ was slurried in 70 mL of THF and 20 mL of methanol and then treated with 0.185 g (0.589 mmol) of (Me₅Si)₂S. The mixture was refluxed for 24 h, resulting in a color change from orange to yellow orange. The crude product was extracted into H₂O and purified as above, giving 0.272 g of [(2)(PF₆)₂] (47% yield).

(e) In THF, with added sulfur: A slurry of 0.50 g (0.628 mmol) of [(CsMe₅)IrCl₂]₂ and 10 mg (0.314 mmol) of S₈ was slurried in 70 mL of THF and 20 mL of methanol and then treated with 0.185 g (0.589 mmol) of (Me₅Si)₂S. The mixture was refluxed for 24 h, resulting in a color change from orange to yellow orange. The crude product was extracted into H₂O and purified as above, giving 0.272 g of [(2)(PF₆)₂] (47% yield).

Crystallography of [(1)(PF₆)₂] and [(2)(PF₆)₂]. Crystals of [(1)(PF₆)₂] were grown by diffusion of hexane into an acetone solution of the cluster. Data were collected on an Oxford Cryosystems Gemini four-circle diffractometer with 0.06 × 0.2 × 0.3 mm mounted on a glass fiber. [(1)(PF₆)₂] crystallizes in the triclinic space group P1 with α = 11.447(4) Å, β = 12.265(6) Å, γ = 20.470(4) Å, α = 91.48(5)°, β = 95.99(4)°, γ = 91.47(4)°, Z = 2, and dcalc = 2.009 g/cm³. 8374 unique reflections were refined to a final R = 0.0595 and Rw = 0.0673. The positions of the iridium and sulfur atoms were obtained by direct methods. The remaining atoms were located by cycles of least-squares refinement and difference Fourier maps using the SHELXLS-76 programs (G. Sheildrick, Nickel XRD, Madison, WI). Both PF₆⁻ anions were disordered in at least two positions, therefore octahedral geometry was imposed on each disordered group and refined between two fractional occupations. Isotropic parameters were refined for F and C atoms, with common P–F and C–C bond lengths refined. The Ir and S atoms were independently refined with anisotropic thermal coefficients. The highest peak in the difference Fourier map corresponding to 2 e⁻ was 0.95 e⁻/Å³. 4831 unique data were refined to a final R = 0.0445 and Rw = 0.0465. The iridium and sulfur positions were deduced by direct methods. The remaining atoms were located by cycles of least-squares refinement and differences Fourier maps using the SHELXLS-76 programs. Hydrogen atoms were introduced at calculated positions, used for structure factor calculations, and refined with common isotropic thermal parameters. Both PF₆⁻ anions were disordered in at least two positions, therefore octahedral geometry was imposed and the constrained groups were refined in two orientations each. Isotropic parameters were refined for F and C atoms, and a common P–F bond length was refined. The remaining atoms were refined anisotropically. The highest peak in the difference Fourier map corresponded to 2 e⁻ in the vicinity of the disordered anions. Selected bond distances and angles are listed in Table 4.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters (25 pages); tables of observed and calculated structure factors (73 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.