

Polyhedral Skeletal Isomerization in the Octanuclear Cluster $[\text{Re}_7\text{IrC}(\text{CO})_{23}]^{2-}$

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Skeletal rearrangements in transition metal cluster compounds provide unique and fascinating examples of stereochemical transformations.¹⁻⁶ However, the understanding of cluster rearrangements for transition metal compounds lags considerably behind that for such main group compounds as the polyhedral boranes and carboranes.⁷⁻¹⁰ This may be in part due to the relatively few established examples of true polyhedral skeletal rearrangements for transition metal cluster frameworks.^{2-4,10} We report evidence for an intramolecular, nondegenerate rearrangement of the octanuclear, mixed-metal cluster compound $[\text{Re}_7\text{IrC}(\text{CO})_{23}]^{2-}$. This example is noteworthy because it is of sufficient symmetry to provide a challenge to current theoretical analyses of transition metal cluster rearrangements^{2,10} and because its energetics may be compared with those of metal atom mobilities on Re/Ir heterometallic surfaces.

Treatment of $[\text{PPN}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{CO})(\text{C}_8\text{H}_{14})]^{11}$ with 1 atm of carbon monoxide readily generates $[\text{PPN}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{CO})_2]$ (**1**), which has the same 1,4-bicapped octahedral structure ($\{\text{Re}_6\text{C}(\text{CO})_{18}\}$ core with one $\mu_3\text{-Re}(\text{CO})_3$ and one $\mu_3\text{-Ir}(\text{CO})_2$ cap in *trans* positions) as its precursor, on the basis of its carbonyl ¹³C NMR spectrum (3:9:9:2 pattern).¹² However, upon prolonged study of the ¹³C NMR sample, a new species, with a 6:3:12:2 pattern of carbonyl signals, was observed to form slowly at room temperature. An X-ray diffraction study of the isolated compound confirmed it as a structural isomer, $[\text{PPN}]_2[\text{Re}_5\text{IrC}(\text{CO})_{17}\{\mu_3\text{-Re}(\text{CO})_3\}_2]$ (**2**).¹³

The structure of the cluster anion is shown in Figure 1. The metal framework is a 1,3-bicapped octahedron, with a single metal atom that is common to the two capped faces. This unique metal center bears two terminal carbonyl ligands, and the remaining vertices have three each. Since the scattering factors of rhenium and iridium are very similar, refinement of the X-ray data did not compel assignment of iridium to the unique metal atom. However, the metal-metal bond distances between the unique position and its six neighbors are shorter on the average (2.876 Å) than the other metal-metal bonds in the cluster (2.996 Å), consistent with the smaller atomic radius for metallic iridium compared to rhenium (1.357 vs 1.370 Å).¹⁴ Furthermore, the ¹³C NMR spectrum shows that the signal for two carbonyls appears at higher field than those for the rest of the carbonyls, which is a typical property of carbonyls bound to iridium vs rhenium.^{11,12} Although carbido-carbonyl clusters are well known for rhenium and osmium as well as for ruthenium and

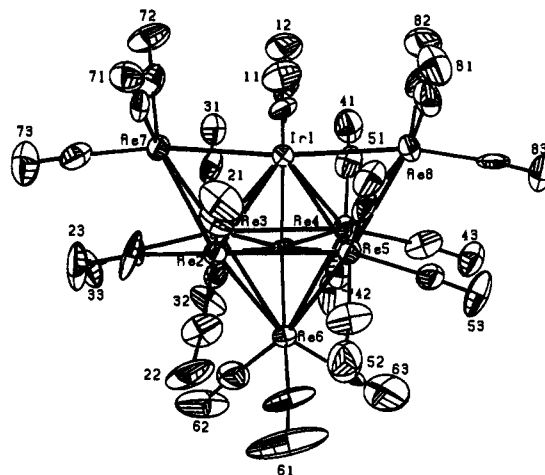


Figure 1. An ORTEP diagram of the cluster anion in $[\text{PPN}]_2[\text{Re}_5\text{IrC}(\text{CO})_{17}\{\mu_3\text{-Re}(\text{CO})_3\}_2]$ (**2**). Metal-metal distances (Å) are as follows: Ir1-Re2 = 2.900(2), Ir1-Re3 = 2.914(1), Ir1-Re4 = 2.877(1), Ir1-Re5 = 2.870(1), Ir1-Re7 = 2.853(1), Ir1-Re8 = 2.884(1), Re2-Re3 = 2.953(1), Re2-Re5 = 3.023(1), Re2-Re6 = 3.098(1), Re2-Re7 = 2.959(1), Re3-Re4 = 2.982(1), Re3-Re6 = 3.066(1), Re3-Re7 = 2.928(1), Re4-Re5 = 2.976(1), Re4-Re6 = 3.056(2), Re4-Re8 = 2.941(1), Re5-Re6 = 3.037(1), Re5-Re8 = 2.931(2). Metal- $\mu_6\text{-C}$ distances (Å) are as follows: Ir1-C = 2.12(2), Re2-C = 2.13(2), Re3-C = 2.08(2), Re4-C = 2.12(2), Re5-C = 2.13(2), Re6-C = 2.07(2).

rhodium,¹⁵⁻¹⁷ there are no known examples among the large clusters of iridium,¹⁸ and **2** is the first structurally characterized compound with a direct iridium-to-interstitial carbon bond. The reasonable Ir-C distance observed in this case suggests that analogous frameworks with a greater number of iridium atoms may be stable as well, once appropriate syntheses are achieved.

(13) (a) Compound **1** (26.8 mg, 0.00830 mmol) in acetone (40 mL) was heated under reflux for 10 h. After removal of the solvent under vacuum, the residue was dissolved in a minimal amount of dichloromethane. 2-Propanol layering and subsequent diffusion gave red needle-shaped crystals (18.4 mg, 64%). Anal. Calcd for $\text{C}_{96}\text{H}_{40}\text{Ir}_7\text{N}_2\text{O}_{23}\text{P}_2\text{Re}_7$: C, 35.71; H, 1.87; N, 0.87. Found: C, 35.47; H, 2.00; N, 0.86. IR (acetone): ν_{CO} 2062 (vw), 2022 (m), 2010 (vs), 1997 (m), 1989 (w, sh), 1977 (w), 1937 (w), 1905 (w), 1981 (w). ¹³C NMR (acetone-*d*₆, 20 °C): δ 415.4 (s, $\mu_6\text{-C}$), 202.0 (s, $\mu_3\text{-Re}(\text{CO})_3$), 196.9 (s, 3C, axial $\text{Re}(\text{CO})_3$), 191.9 (s, 12C, eq $\text{Re}(\text{CO})_3$), 168.8 (s, 2C, $\text{Ir}(\text{CO})_2$). (b) Crystallographic data for **2**: monoclinic, space group $P2_1/c$, $a = 28.023(2)$ Å, $b = 17.030(1)$ Å, $c = 20.237(1)$ Å, $\beta = 98.15(1)^\circ$, $V = 9560(2)$ Å³, $Z = 4$. (c) Diffraction data collection was carried out at 27 °C on a Syntex P2₁ automated diffractometer. A total of 6289 reflections with $I > 2.58\sigma(I)$ were measured, corrected for absorption (μ (Mo K α) = 104.65 cm⁻¹; maximum/minimum transmission factor = 0.363/0.136), and used for solving the structure by direct methods (SHELX-86). Correct positions for the metal atoms were deduced from an *E*-map. Subsequent least-squares refinement and difference Fourier syntheses revealed positions for the remaining non-hydrogen atoms. The phenyl rings, including hydrogen atoms, were refined as rigid idealized groups. The cluster anion and the PPN^+ cations were refined in isolated blocks. In the final cycle of least-squares refinement, common isotropic thermal parameters were varied for the hydrogen atoms, anisotropic thermal coefficients were refined for Ir, Re, P, O, and cluster C atoms, and the remaining atoms were refined with independent isotropic thermal coefficients. The highest peaks in the final difference Fourier map suggested a minor rotational disorder for Re6 carbonyl ligand positions. Final agreement factors were $R = 0.050$, $R_w = 0.055$. The use of Re scattering factors at position Ir1 gave equivalent final agreement factors (slightly but not significantly larger).

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Compound **2** also joins the relatively short list of octanuclear compounds that display the 1,3-bicapped octahedral structure.¹⁷

The kinetics of the rearrangement **1** → **2** in 2-butanone was studied by following the disappearance of the 462-nm absorption peak in the visible spectrum of **1**. Clean first-order kinetics was observed, and there was no change in the derived rate when the reaction was conducted under an atmosphere of carbon monoxide or in the presence of a nitrogen purge. The rate constants were $3.8(4) \times 10^{-4} \text{ s}^{-1}$, $1.2(1) \times 10^{-4} \text{ s}^{-1}$, and $3.0(3) \times 10^{-5} \text{ s}^{-1}$ at 78, 69, and 59 °C, respectively. The derived activation parameter values are $\Delta H^\ddagger = 30.5(5) \text{ kcal/mol}$ and $\Delta S^\ddagger = 13(2) \text{ cal/mol}\cdot\text{K}$. Interestingly, very similar values of $\Delta H^\ddagger = 28.7(1) \text{ kcal/mol}$ and $\Delta S^\ddagger = 13(4) \text{ cal/mol}\cdot\text{K}$ were determined for the isomerization of $\text{Os}_6\text{Pt}(\text{CO})_{17}(\mu_3\text{-NCMe})(\text{C}_8\text{H}_{12})$ to $\text{Os}_6\text{Pt}(\text{CO})_{17}(\mu_4\text{-NCMe})(\text{C}_8\text{H}_{12})$, a process which must involve substantial reorganization of the metal framework in the transition state(s) relating these two relatively open structures.¹⁹

The energetics of making and breaking Re/Ir bonds involved in the rearrangement **1** → **2** may be compared with observations on rhenium–iridium heterometallic surfaces.^{20,21} A recent report has shown that an adsorbed rhenium atom on a (001) iridium surface will first extract an iridium atom from the substrate to form a heterometallic dimer, then drop into the surface vacancy, leaving the iridium atom as an adsorbate. The activation energies measured were 15 kcal/mol for dimer formation and 22 kcal/mol for dimer dissociation.²¹ This indication that heterometallic Re–Ir bonds are stronger than homometallic Ir–Ir bonds is consistent with other data on bimetallic surfaces, which has been interpreted in terms of charge transfer between the dissimilar elements.²² A driving force for the rearrangement **1** → **2** may be the increased number of Re–Ir bonds; however, contributions to the energetics from ligand effects, either the external carbonyls or the internal carbide, cannot be discounted.

The skeletal rearrangements observed for polyhedral boranes and carboranes have been analyzed in terms of the application of diamond–square–diamond (DSD) processes.^{2,3,7–10} The rearrangement **1** → **2** may be accomplished via single DSD steps, but these sequences pass through pentagonal bipyramidal structures that should have an extra two electrons.² (Note that *cis/trans* isomerization of octahedral $[\text{Rh}_2\text{Fe}_4\text{B}(\text{CO})_{16}]^-$ occurs by an *associative* pathway, with the added ligand presumably stabilizing a pentagonal pyramid geometry.⁴) However, as shown in Figure 2, an unsaturated intermediate may be avoided by application of a simultaneous *double* DSD process, which produces a 1,2-bicapped octahedral species in one step. A second application of the double DSD gives the observed 1,3-bicapped product **2**. Interestingly, as shown on the left-hand side of Figure 2, application of the same individual DSD processes, but in a different order, proceeds through a relatively symmetrical hexagonal bipyramidal structure. This structure formally requires nine skeletal bonding pairs instead of the seven associated with the capped octahedral structures, but the highest occupied orbitals may be nearly degenerate and so near the nonbonding level that

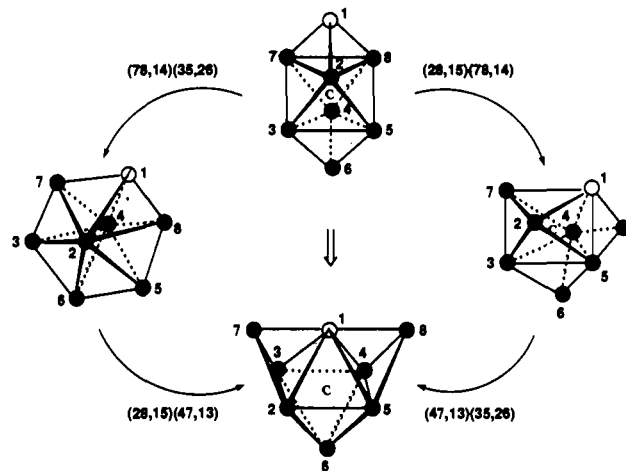


Figure 2. Two possible pathways for the rearrangement **1** → **2** that involve sequences of simultaneous diamond–square–diamond (DSD) steps. The designation (28, 15) indicates that the 2–8 bond breaks and a 1–5 bond forms.

two missing electron pairs may not cost too much energy.² Further theoretical analysis is required before either of these or another possible pathway is supported.

Unfortunately, an experimental attempt to provide mechanistic evidence failed: rhenium center 6 retains a unique relationship with iridium center 1 along the pathways shown in Figure 2, and this center may be “labeled” by exposing **1** to ^{13}CO , which enriches all metal centers except the capping center (6).¹² However, the ^{13}C NMR spectrum of **2** generated from selectively enriched **1** showed an equal distribution of ^{13}CO . Thus, although neither **1** nor **2** shows evidence for carbonyl scrambling, at least one intermediate must allow it.

We have observed that one of the two $\text{Re}(\text{CO})_3$ caps in **2** can be removed by heating in acetonitrile to form $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$ and that another capping group can then be introduced to form a mixed-trimetallic cluster. This heterometallic “label” will allow us not only to study the regioselectivity of reactions apparently occurring at the capping metal center^{12,23} but also to probe more deeply for polyhedral rearrangements that may occur with these octanuclear frameworks.

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Supplementary Material Available: Tables of the details of crystallographic data collection, atomic coordinates, thermal parameters, and selected bond distances and angles for $[\text{PPN}]_2[1,3\text{-}\{\mu_3\text{-Re}(\text{CO})_3\}_2\text{Re}_5\text{IrC}(\text{CO})_{17}]$ (**2**) (11 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.

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