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Communication

Dynamic Permutational Isomerism in a closo-Cluster**

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<pictid> Supporting information (detailed experimental procedures for the syntheses of **1^a**/**2^a--4^a**/**4^b**, spectroscopic and X-ray crystallographic characterization data, kinetic data, and nonlinear absorption data) and the ORCID identification number for the author of this article can be found under <url>http://dx.doi.org/10.1002/chem.201600550</url>.

Cluster compounds: Permutational isomers $[W_2RhIr_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ interconvert in solution by a cluster metal vertex exchange (see scheme); they display differing chemical and physical properties, replacement of CO by PPh_3 occurring at one permutational isomer only, while the isomers display distinct optical power limiting behavior.

Transition Metals

carbonyl ligands

cluster compounds

heterometallic complexes

isomers

transition metals

Permutational isomers of trigonal bipyramidal $[W_2RhIr_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ result from competitive capping of either a W_2Ir or a WIr_2 face of the tetrahedral cluster $[W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ from its reaction with $[Rh(CO)_2(\eta^5\text{-}C_5HMe_4)]$. The permutational isomers slowly interconvert in solution by a cluster metal vertex exchange that is proposed to proceed by Rh<C->Ir and Rh<C->W bond cleavage and reformation, and via the intermediacy of an edge-bridged tetrahedral transition state. The permutational isomers display differing chemical and physical properties: replacement of CO by PPh_3 occurs at one permutational isomer only, while the isomers display distinct optical power limiting behavior.

Isomerism has been a key concern of chemists since von Liebig and Wöhler isolated silver fulminate and silver cyanate.[1] Isomers may possess dramatically different biological or materials properties, and so understanding isomerism and controlling isomer distribution are critically important concerns in contemporary chemistry. The two main classes of isomers, structural isomers and stereoisomers, can be further classified as chain (skeletal), positional, and functional-group isomers for the former, and enantiomers and diastereomers for the latter. Polyhedra abound in inorganic chemistry and in theory offer possibilities for positional (permutational) isomerism from exchange of vertex atoms that are not readily available in the purely organic domain. Despite this promising possibility, "reversible cluster core isomerism remains a rare phenomenon".[2] The smallest closo polyhedron with distinguishable vertices is the trigonal bipyramid, with two three-connected apical vertices and three four-connected equatorial vertices, and thus interchange of different atoms occupying these distinct vertex types in a trigonal bipyramidal cluster constitutes the archetypal polyhedral permutational isomerism. We demonstrate herein the use of the capping reagent $[Rh(CO)_2(\eta^5\text{-}C_5Me_4H)]$ in the construction of the first examples of tungsten--rhodium--iridium clusters, report the syntheses and crystallographic confirmation of permutational isomers with a trigonal bipyramidal core framework, describe kinetic studies that define the rate of their interconversion, suggest a mechanism for their isomerization, and disclose preliminary studies of their chemical and physical properties: phosphine substitution is permutational-isomer-specific, while linear optical and nonlinear optical behavior is isomer-distinct.

The reaction of $[W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ with an excess of $[Rh(CO)_2(\eta^5\text{-}C_5HMe_4)]$ in refluxing CH_2Cl_2 afforded three clusters following TLC: isomers $[W_2RhIr_2(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**1^a**, dark green) and $[W_2RhIr_2(\mu\text{-}CO)_4(CO)_5(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**2^a**, red), together with $[W_2Rh_2Ir_2(CO)_8(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)_2]$ (**3^a**, black; Scheme^^1<schr1>: see the Supporting Information for synthetic and spectroscopic characterization details). Clusters **1^a** and **2^a** were conclusively identified by single-crystal X-ray diffraction studies, while the structure of **3^a** was definitively assigned following a structural study of its molybdenum-containing analogue (see below), comparison of IR and ^{1}H^^NMR data, and examination of its ESI MS data (Figure^^S1, Supporting Information). Clusters **1^a** and **2^a** both possess trigonal bipyramidal core geometries; one tungsten atom is at an apical site and the other at an equatorial site in **1^a** (Figure^^1<figr1>, top), while both tungsten atoms are located at equatorial sites in **2^a** (Figure^^1<xfigr1>, bottom). Clusters **1^a** and **2^a** each possess 72^^cluster valence electrons, and are EAN-precise for M_5 clusters with nine M<C->M bonds. Note that there is electronic asymmetry in both **1^a** (W5, 17e; Rh4, 19e) and **2^a** (W1, 17e; Rh4, 19e). The bond lengths and angles in both clusters are unexceptional.

The analogous reaction of $[Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2]$ with excess $[Rh(CO)_2(\eta^5\text{-}C_5HMe_4)]$ in refluxing CH_2Cl_2 proceeded similarly to afford pentanuclear clusters $[Mo_2RhIr_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**1^b**/**2^b**) and a hexanuclear cluster $[Mo_2Rh_2Ir_2(\mu_3\text{-}CO)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)_2]$ (**3^b**) (Scheme S1: see the Supporting Information for synthetic and spectroscopic characterization details). In contrast to the tungsten-containing reaction, the **1^b**/**2^b** mixture was not separable by TLC; however, **1^b** could be crystallized from the mixture (Figure^^S2, Supporting Information) and was shown to be isostructural with **1^a**, while spectroscopic data are consistent with **2^b** possessing an analogous structure to **2^a**. The single-crystal X-ray diffraction study of **3^b** (Figure^^2<figr2>) reveals two $[Rh(\eta^5\text{-}C_5HMe_4)]$ caps on a Mo_2Ir_2 tetrahedral core, one at each of the Mo_2Ir and $MoIr_2$ faces that are capped to afford the pentanuclear isomers. The intracluster M<C->M bond lengths of **3^b** are not unusual. The cluster possesses 84 CVE, the

EAN-predicted electron count for a bicapped tetrahedron. Despite their structures corresponding to the addition of the two alternative [Rh(η^5-C_5HMe_4)] caps found on the pentanuclear permutational isomers, the hexanuclear clusters do not arise from stepwise addition of [Rh(η^5-C_5HMe_4)] units. Reactions of **1^a** and **2^a** with excess [Rh(CO)$_2$(η^5-C_5HMe_4)] in refluxing CH_2Cl_2 returned unreacted starting cluster, higher boiling point solvents resulting in decomposition of the rhodium reagent only, while reaction of [$W_2Ir_2(CO)_{10}$(η^5-C_5H_5)$_2$] with a much greater excess of [Rh(CO)$_2$(η^5-C_5HMe_4)] afforded higher yields of **3^a**; this is suggestive of synthesis of **3^a** proceeding by an unusual termolecular pathway, but further comment is unwarranted.

The ^{1}H^^NMR spectra of the **1^b**/**2^b** mixture at room temperature display resonances at δ=5.21, 5.19, 5.14, and 5.10^^ppm (integrated intensities 2:1:2:1), corresponding to the four cyclopentadienyl ligands of the two isomers. These resonances arise from interconverting isomers rather than chromatographically inseparable noninterconverting species; dissolution of crystals of **1^b** immediately re-established the **1^b**/**2^b** equilibrium at its precrystallization value (Figure^^S3, Supporting Information). The chromatographically-separated tungsten-containing isomers **1^a** and **2^a** similarly interconvert, but at a significantly reduced rate that is amenable to spectroscopic interrogation. Thus, solution IR spectra in the ν(CO) region can be employed to monitor establishment of the equilibrium (Figure^^S4 and S5, Supporting Information), the isosbestic points suggesting reversible first-order kinetics. In contrast, solid-state IR spectra of **1^a** and **2^a** are invariant over time, even with heating, while unit-cell parameters of crystals of **1^a** and **2^a** did not change over a one year period; the isomerization is thus restricted to the liquid phase. The solution UV/Vis spectra are broad and relatively featureless (Figure^^S6, Supporting Information), but a distinct color change is apparent as CH_2Cl_2 solutions of **1^a** and **2^a** progressively establish the **1^a**/**2^a** equilibrium (Figure^^S7, Supporting Information); solutions in CH_3CN, MeOH, acetone, THF, toluene, and *n*-hexane display the same behavior. The experimental data from high-resolution ^{1}H^^NMR studies were found to be suitable for monitoring the interconversion of **1^a** and **2^a** and obtaining kinetic and thermodynamic parameters, due to

good separation of resonances leading to consistent integrations. Typical time-dependent spectra for the isomerization of **1^a** and **2^a** in $CDCl_3$, [D3]acetontrile, [D_6]acetone, and [D_8]toluene at 30--35^°C are presented in Figures^^S8--S12, time evolution of the relative populations of **1^a** and **2^a** are given in Figure^^S13--S15, Supporting Information, and Eyring, van't^^Hoff, and relative activation energies plots are presented in Figures^^S16--S18, Supporting Information. The resultant thermodynamic and kinetic values are presented in Tables^^S4 to S9, Supporting Information. The rate constants k_1 and $k_{<M->1}$ (Table^^S4, Supporting Information) indicate that the isomerization of **1^a** to **2^a** is a slow process in various solvents at 30^°C, accelerating with an increase in the temperature (Table^^S9, Supporting Information). This observation is consistent with the activation parameters derived from Eyring plots (Figures^^S16--S17 and Tables^^S8 and S9, Supporting Information), which suggest a slow process involving a substantial structural reorganization in the transition state.[3] In $CDCl_3$ the isomerization leads to similar equilibrium constants K_{eq} at the different temperatures (ca. 1.8) and with **2^a** being the dominant species at the equilibrium. Contrasting behavior is observed in the more polar solvents [D_6]acetone and [D_3]acetonitrile, with **1^a** being the dominant species at the equilibrium and a decrease in K_{eq} with temperature increase. A similar behavior is noted with isomerization rate, the isomerization of **1^a** to **2^a** in $CDCl_3$ being slower than in [D_6]acetone and [D_3]acetonitrile (Table^^S9, Supporting Information), and suggesting that the solvent polarity plays an important role in stabilization of the intermediate in the solution. $\Delta G_1^{\ddagger}$ and $\Delta G_{-1}^{\ddagger}$ values ($CDCl_3$, 298^^K, 101.12±1.50 and 102.63±1.56^^kJ^mol$^{<M->1}$, respectively: Table^^S5, Supporting Information) are greater than typical values for intramolecular processes such as ligand migration about cluster cores (for which activation energies usually fall within the range ~20--80^^kJ^mol$^{<M->1}$),[4] which is consistent with a significant structural reorganization involving metal sites exchanging and carbonyl ligands migration.

Cross-over experiments of **1^a** and [$Mo_2RhIr_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$] in $CDCl_3$ and CD_3CN did not show resonances corresponding to [$W_2RhIr_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$] after five days; only **1^a**, **2^a** and [$Mo_2RhIr_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$] were seen,

consistent with the isomerization proceeding by an intramolecular process. Theoretical studies of trigonal bipyramidal (tbp) organometallic clusters have demonstrated that diamond-square-diamond (DSD) and edge-cleavage rearrangements are the two common intramolecular polyhedral rearrangement pathways.[5] A single DSD process proceeds from a tbp to an intermediate square-pyramid state and then on to a tbp; this results in two apical atoms of the initial tbp moving to equatorial sites. The presence of an apical Rh atom in both **1^a** and **2^a** therefore rules out a single-DSD mechanism, and suggests an edge-cleavage pathway. Dynamic polyhedral rearrangements of mixed-metal clusters usually involve heterometallic rather than homometallic bond cleavage/formation,[6] so a pathway from **1^a** to **2^a** that involves cleavage of a Rh<C->Ir bond and subsequent formation of a Rh<C->W bond is likely (Figure^^3<figr3>). Support for such Rh-localized bond cleavage/formation is provided by the [Ir(η^5-C_5HMe_4)]-capped analogues; the cores of the isomers [W_2Ir_3(μ-CO)$_3$(CO)$_6$(η^5-C_5H_5)$_2$(η^5-C_5HMe_4)] and [W_2Ir_3(μ-CO)$_4$(CO)$_5$(η^5-C_5H_5)$_2$(η^5-C_5HMe_4)] are isostructural with **1^a** and **2^a**, respectively, but no interconversion was observed by NMR spectroscopy,[7] presumably a result of the stronger analogous Ir<C->Ir and Ir<C->W bonds.

Preliminary studies of the chemical and physical properties of the permutational isomers **1^a** and **2^a** were then undertaken. Reaction of PPh_3 with **2^a** at room temperature proceeded slowly and by two pathways: isomerization between **1^a** and **2^a**, and phosphine substitution (Figures^^S19--S20, Supporting Information). After five^^days, the isomerization reached a dynamic equilibrium at room temperature (ratio **1^a**/**2^a** 1:1.35) while ligand substitution was still proceeding slowly. This **1^a**/**2^a** ratio is smaller than that from the isomerization reaction between **1^a** and **2^a** (1:1.835), consistent with reaction of **2^a** with PPh_3 depleting its concentration. Addition of PPh_3 to **1^a** resulted in the same outcome (Figures^^S21--S22, Supporting Information). Heating the reaction mixtures afforded [W_2Ir_2Rh(μ-CO)$_4$(CO)$_4$(PPh_3)(η^5-C_5H_5)$_2$(η^5-C_5HMe_4)] (**4^a**) only, characterized by spectroscopic means and a single-crystal X-ray diffraction study (Figure^^4<figr4>). The structural study of **4^a** revealed the same core geometry as **2^a** and ligand substitution at the apical iridium; bond lengths are unexceptional (Table^^S3, Supporting Information). The

analogous reactions of PPh_3 with **1^b** and **2^b** in refluxing THF afforded [$Mo_2Ir_2Rh(\mu$-$CO)_4(CO)_4(PPh_3)(\eta^5$-$C_5H_5)_2(\eta^5$-$C_5HMe_4)$] (**4^b**) (Figure^^S23, Supporting Information), which is isostructural with **4^a**, and which, in combination with the outcome from the aforementioned tungsten-containing clusters, suggests **2^b**-centered reactivity. This ligand substitution chemistry is therefore permutational isomer-specific.

Metal clusters have attracted interest for potential optical limiting applications,[8] but we are not aware of prior assessment of optical limiting properties of permutational isomers. The linear optical absorption properties of **1^a** and **2^a** in CH_2Cl_2 solvent are distinct (Figure^^S6--S7, Supporting Information); **1^a** is dark green and **2^a** is dark red. The UV/Vis spectra of the permutational isomers contain low-intensity bands through the visible region, suggestive of potential as broad-band optical limiters. Relevant data for optical limiting merit at the benchmark wavelength of 532, 570, and 630^^nm are collected in Table^^S10, Supporting Information. The excited-state cross sections σ_{eff} of the clusters at the three wavelengths are slightly larger than the respective ground-state cross sections σ_0; although the optical-limiting performance is weak in an absolute sense, the clusters display different optical limiting behavior. While little difference is seen in clamping fluence at 570^^nm (0.13^^J^cm$^{<M->1}$, Figure^^S24, Supporting Information), **2^a** shows the better performance at 532^^nm (0.082^^J^cm$^{<M->1}$) and **1^a** performs better at 630^^nm (0.060^^J^cm$^{<M->1}$). The differences in linear absorptivity are reflected in differing effective two-photon absorption coefficients β_{eff} (Figure^^S25--S26, Supporting Information), for which a stronger linear absorption tends to give a smaller cross section. Cluster **2^a** shows the larger effective two-photon absorption cross-section at 532^^nm (ca. 1.9×10^5^^cm^W$^{<M->1}$), whereas the value for **1^a** is larger at 630^^nm (ca. 1.7×10^5^^cm^W$^{<M->1}$).

Although examples of skeletal,[9] functional-group,[10] and permutational[11] transition-metal cluster isomers are extant, the present study is unusual in affording an example of dynamic permutational isomerism with the smallest closo-cluster core for which vertices are distinguishable. Examples of reversible cluster-core isomerism for which kinetic data are available are rare.[9c--f,^11a,b,^12] In the current work, kinetic and thermodynamic data and

experimental studies support a permutational isomerism mechanism involving interchange between two trigonal bipyramidal cores by an edge-bridged tetrahedral transition state; the weaker Rh<C->M bonds in these heterotrimetallic clusters are suggested as the sites of bond cleavage/formation. The present studies have also afforded the opportunity to contrast the chemical and physical properties of permutational isomers. The permutational isomers have distinct linear optical properties and differing optical power limiting performance. Iridium is the preferred site of ligand substitution at Group^^6 metal-iridium clusters,[13] and phosphine substitution is restricted in the current system to the permutational isomer with the sterically accessible apical iridium atom.

Experimental Section

Detailed experimental procedures for the syntheses of **1^a/2^a--4^a/4^b**, spectroscopic and X-ray crystallographic characterization data, kinetic data, and nonlinear absorption data are reported in the Supporting Information.

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Scheme^^1 Synthesis of $[W_2RhIr_2(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**1^a**), $[W_2RhIr_2(\mu\text{-}CO)_4(CO)_5(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**2^a**), and $[W_2Rh_2Ir_2(CO)_8(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)_2]$ (**3^a**).

Figure^^1 ORTEP plots and atom numbering schemes for $[W_2RhIr_2(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**1^a**)^^(top) and $[W_2RhIr_2(\mu\text{-}CO)_4(CO)_5(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**2^a**)^^(bottom). Displacement ellipsoids are shown at the 40^% probability level. Hydrogen atoms have been omitted for clarity.

Figure^^2 ORTEP plot and atom numbering scheme for $Mo_2Rh_2Ir_2(\mu_3\text{-}CO)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)_2$ (**3^b**). Displacement ellipsoids are shown at the 40^% probability level. Hydrogen atoms and the lattice methanol molecule have been omitted for clarity. Selected bond lengths [Å]: Mo1<C->Ir2: 2.7422(8), Mo1<C->Ir3: 2.8121(10), Mo1<C->Rh4: 2.8080(8), Mo1<C->Mo5: 2.8847(8), Mo1<C->Rh6: 2.7173(8), Ir2<C->Ir3: 2.7377(9), Ir2<C->Rh4: 2.6972(8), Ir2<C->Mo5: 2.7484(7), Ir3<C->Rh4: 2.7374(8), Ir3<C->Mo5: 2.8309(7), Ir3<C->Rh6: 2.7908(9), Mo5<C->Rh6: 2.7915(10), Mo1<C->C16: 1.996(4), Ir2<C->C21: 1.880(4), Ir2<C->C22: 1.901(4), Ir2<C->C25: 2.326(4), Ir2<C->C234: 2.319(4), Ir3<C->C31: 1.899(4), Ir3<C->C32: 1.874(4), Ir3<C->C234: 2.116(4), Rh4<C->C234: 2.008(4), Mo5<C->C25: 2.012(4), Mo5<C->C56: 1.990(4), Rh6<C->C16: 2.224(4), Rh6<C->C56: 2.191(4).

Figure^^3 Proposed mechanism for **1^a** to **2^a** intercoversion (metal cluster core atoms only).

Figure^^4 ORTEP plot and atom numbering scheme for $[W_2Ir_2Rh(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)]$ (**4^a**). Displacement ellipsoids are shown at the 40^% probability level. Hydrogen atoms have been omitted for clarity.