susceptibility vs temperature from 1.8 to 250 K shows (Figure 2) typical antiferromagnetic behavior for I and III with maxima at ~19 and ~9 K. A preliminary fit of the magnetic data for I has been obtained by using a derived[12] equation based on the Heisenberg model for spin–spin interactions ($E(S) = -JS_1S_2$) in a coupled $S = {}^5/_2/S = {}^5/_2$ system. The derived coupling constant J is -5.0 cm^{-1} for $g = 2.00$. A satisfactory fit could not be obtained by using the same model for III, presumably due to the single-ion anisotropy for a Co(II) ion. However, the temperature dependence of the magnetic susceptibility suggests that J is between 0 and -10 cm^{-1}. A maximum in the χ vs T curve for II was not found within the temperature range studied. The lack of significant magnetic coupling, suggested by the magnetic studies, also is apparent in the ^{57}Fe Mössbauer spectrum of II. The spectrum at 4.2 K in an applied magnetic field of 7.8 kG indicates very weak coupling (if any at all!) between the two irons. The zero-field spectrum at 4.2 K shows a sharp doublet with an isomer shift of 1.00 (1) mm/s (vs Fe at room temperature) and a quadrupole splitting of 2.40 (1) mm/s. The IS value is similar to the one reported[13] for the $(FeCl_4)^{2-}$ complex (1.01 mm/s).[14]

The EPR spectrum of I in DMF solution shows a six-line spectrum with a nuclear hyperfine splitting of 81.6 G and indicates that the dimer undergoes solvolysis and dissociates to a monomeric Mn(II) species. This dissociation very likely occurs in coordinating solvents with the other members of the $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ series as well and should be taken into account in the evaluation of the solution properties of these compounds. Cyclic voltammetric studies in CH_3CN solution show irreversible oxidation waves for I and III and a reversible wave for II ($E_{1/2} = +0.08$ V vs SCE). The solvolytic dissociation of the dimers in donor solvents makes it difficult to identify the exact nature of the electroactive species in solutions of II. The electronic spectrum of III in CH_3CN solution is typical of tetrahedrally coordinated Co(II) with transitions at 658 (sh), 644, 630 (sh), 560, 534 (sh), 360 (sh), and 278 nm.

The $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ anions are ideally suited as reagents for the synthesis of other dinuclear complexes by substitution of the chloride ligands in metathetical reactions. This synthetic utility already has been demonstrated in reactions of the $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ dimers with $AgNO_3$ and the formation of the $[M_2(NO_3)_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ dimers[16] (M = Mn, Co). The structures of these new dimers have been determined and show $[M_2(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2+}$ cores very similar to those in the chloro analogues.

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Supplementary Material Available: Tables SI and SII, listing positional and thermal parameters of all atoms in the asymmetric unit of $(Et_4N)_2[Mn_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ (4 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48109

D. Coucouvanis*
K. Greiwe
A. Salifoglou
P. Challen

Nuclear Research Center "Demokritos"
Aghia Paraskevi, Attiki, Greece

A. Simopoulos
A. Kostikas

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Photoreactions of $Ir_8(CO)_{22}^{2-}$. Homolytic Cleavage of an Unsupported Metal–Metal Bond Linking Two Tetrahedral Iridium Carbonyl Clusters

Sir:

The photoreactions of dinuclear metal complexes linked by a metal–metal single bond have been subject to considerable attention over the past decade.[1-6] An example is $Mn_2(CO)_{10}$ for which photolysis leads to competitive reactions: homolytic cleavage of the metal–metal bond and dissociation of CO.[1,7] The former, which results from excitation of $\sigma_{MM} \rightarrow \sigma^*_{MM}$ and/or $\pi_{ML} \rightarrow \sigma^*_{MM}$ transitions, gives mononuclear 17-electron metal radical intermediates, i.e.

$$L_xM\text{–}ML_x \xrightarrow{h\nu} 2L_xM^\bullet \tag{1}$$

Described here is a previously unexplored elaboration of this theme to a case where the metal–metal bond photolyzed links two polyhedral metal clusters. The specific example is the octairidium anion $Ir_8(CO)_{22}^{2-}$, which consists of two $Ir_4(CO)_{11}^-$ tetrahedra linked by a metal–metal single bond unsupported by bridging ligands.[8] It is shown here that photolysis of this remarkable polynuclear species apparently leads to homolytic bond cleavage to give the reactive cluster radical anion $Ir_4(CO)_{11}^-$.

The electronic spectrum of the PPN^+ salt ($PPN^+ = N(PPh_3)_2^+$)[9] of $Ir_8(CO)_{22}^{2-}$ in methylene chloride solution displays an intense absorption band at 532 nm ($\epsilon = 1.68 \times 10^4$ M^{-1} cm^{-1}, Figure 1). Since no visible range bands are apparent in the electronic spectra of the tetrahedral clusters $Ir_4(CO)_{12}$ or $HIr_4(CO)_{11}^-$,[10,11] we have assigned this band as a $\sigma_{MM} \rightarrow \sigma^*_{MM}$ orbital transition localized to the bond linking the two clusters in analogy to the strong $\sigma_{MM} \rightarrow \sigma^*_{MM}$ absorption bands of dinuclear complexes such as $Mn_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$.[1,12]

Solutions of $[PPN]_2[Ir_8(CO)_{22}]$ under CO in various solvents were observed to be indefinitely stable in the dark; however, exposure even to ambient room light resulted in rapid conversion to yellow solutions. The product of quantitative 520 nm photolysis in dichloromethane solution under N_2 (Figure 1) was shown to be the chlorotetrairidium anion $Ir_4(Cl)(CO)_{11}^-$ by comparing the IR and UV–vis spectra to those of an authentic sample[13] under identical conditions. Analogous 520-nm photolysis in CH_2Cl_2

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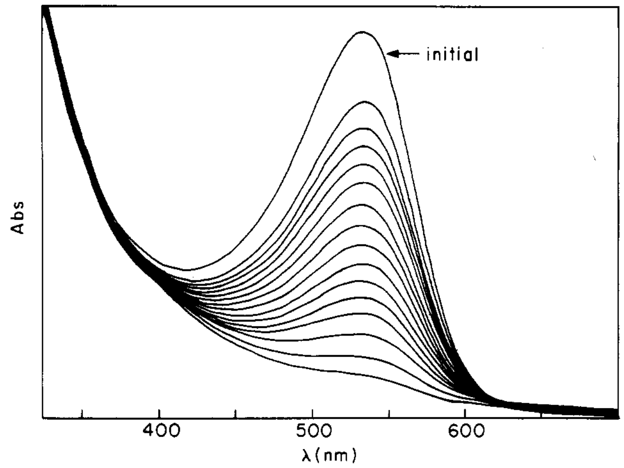

Figure 1. Spectrum of $(PPN)_2[Ir_8(CO)_{22}]$ (6.2×10^{-5} M) in methylene chloride under N_2 and successive spectra recorded periodically during photolysis at 520 nm.

solution but under CO (1 atm) led instead to quantitative formation of $Ir_4(CO)_{12}$ as the final product. However, it was independently demonstrated that $Ir_4(Cl)(CO)_{11}^-$ reacts with CO under these conditions to form $Ir_4(CO)_{12}$ at a rate consistent with the latter being the only product observable under the photolysis conditions. The quantum yield for disappearance (ϕ_d) of the strong absorbance at 532 nm in CH_2Cl_2 proved to be essentially independent of whether N_2 or CO was the blanketting atmosphere, the values being 0.37 ± 0.02 and 0.40 ± 0.02 mol/einstein, respectively.[14]

Abstraction of a chlorine from the chlorocarbon solvent is consistent with the expected reactivity for a metal radical and suggests that the photoreaction products result from the following sequence of events:

$$Ir_8(CO)_{22}^{2-} \xrightarrow{h\nu} 2Ir_4(CO)_{11}^- \qquad (2)$$

$$Ir_4(CO)_{11}^- + CH_2Cl_2 \rightarrow Ir_4(Cl)(CO)_{11}^- + CH_2Cl^\bullet \qquad (3)$$

$$Ir_4(Cl)(CO)_{11}^- + CO \rightarrow Ir_4(CO)_{12} + Cl^- \qquad (4)$$

The fate of the organic radical was not determined.

The ability of the apparent $Ir_4(CO)_{11}^-$ intermediate to abstract a chlorine atom from dichloromethane is an indication of the relative reactivity of this cluster anion. Although trapping with chlorocarbons is common for metal radicals, dichloromethane is a poor chlorine donor. For example, quantiative studies of the tungsten radical $(\eta^5\text{-}C_5H_5)W(CO)_3$,[2] have shown its reactivity with CH_2Cl_2 to be less than 10^{-4} of that with CCl_4;[2] for the manganese radical $Mn(CO)_3(P(i\text{-}Bu_3))_2$, the reactivity ratio is about 10^{-6}.[7d] Although low reactivity for $Ir_4(CO)_{11}^-$ toward CH_2Cl_2 might have been anticipated if the unpaired electron were delocalized over the cluster tetrahedron, this tendency may be counteracted by the anionic charge, which would increase the reducing nature of the cluster.

A particularly surprising result was the observation that the 520-nm photolysis of the $\sigma_{MM} \rightarrow \sigma^*_{MM}$ band of the octairidium complex in tetrahydrofuran solution under CO leads to the formation of $HIr_4(CO)_{11}^-$, the apparent product of hydrogen abstraction from an organic donor. The quantum yield ϕ_d was 0.2, about half that measured in CH_2Cl_2 under otherwise comparable conditions, but nonetheless quite substantial. The origin of the hydrogen is as yet uncertain and is the subject of continuing investigation. However, 520-nm photolysis of the potassium salt $K_2[Ir_8(CO)_{22}]$ under otherwise identical conditions also gives $HIr_4(CO)_{11}^-$ with virtually the same ϕ_d, suggesting that the tetrairidium radical may be sufficiently reactive to abstract a hydrogen atom from THF.

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Department of Chemistry
University of California
Santa Barbara, California 93106

David M. Vandenberg
Alan E. Friedman
Peter C. Ford*

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(14) Quantitative photolyses were carried out for carefully deaerated solutions prepared with vacuum-like techniques using photochemical apparatus and Reinecke ion actinometry.

Core Conversion Reactions of Iron–Sulfur Clusters: Topological Isomer of the Fe_6S_6-Prismane Core

Sir:

High-nuclearity transition-metal chalcogenide clusters very frequently contain highly symmetric cores $[M_xE_y]^z$ (E = S, Se) stabilized by terminal halide (X), aryloxide, or thiolate ligands, as in, e.g., $[Fe_6S_6X_6]^{2-,3-}$ (**1**),[1,2] $[Co_8S_6(SPh)_8]^{4-,5-}$,[3] $[Fe_8S_6I_8]^{3-}$ (**2**),[4] and $[M_2Fe_6S_6(CO)_6X_6]^{3-,4-}$ (M = Mo, W).[5] Recent work in this laboratory and elsewhere has demonstrated that the use of tertiary phosphines as ligands can lead to the formation of new $[M_xE_y]^z$ core structural types not yet encountered in the absence of these ligands. Examples include *closo*-$[Fe_6S_8(PEt_3)_6]^{+,2+}$,[6] $[Co_6E_8(PR_3)_6]^{0,+}$,[7] and $[Ni_8S_6(PPh_3)_6Cl_2]$,[8] and the *nido* topological versions of **2**, $[Fe_7S_6(PEt_3)_4Cl_3]$[9] (**3**) and $[Co_7S_6(PPh_3)_5Cl_2]$.[10] In the course of our investigations of new routes to high-nuclearity iron–sulfur clusters as potential building blocks for homo- and heterometal clusters and their topological relationships,[9] we have developed the facile reductive core conversion reaction

$$\underset{\mathbf{4}}{[Fe_4E_4L_4]^{2-}} \text{ or } \underset{\mathbf{1}}{[Fe_6S_6L_6]^{3-}} \xrightarrow[\text{MeCN}]{2[Fe(PEt_3)_2L_2]} \underset{\mathbf{5,\ 6}}{[Fe_6E_6(PEt_3)_4L_2]}$$

(L = halide, PhS^-), affording clusters with the previously unknown core $[Fe_6S_6]^{2+}$ in good purified yields.

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