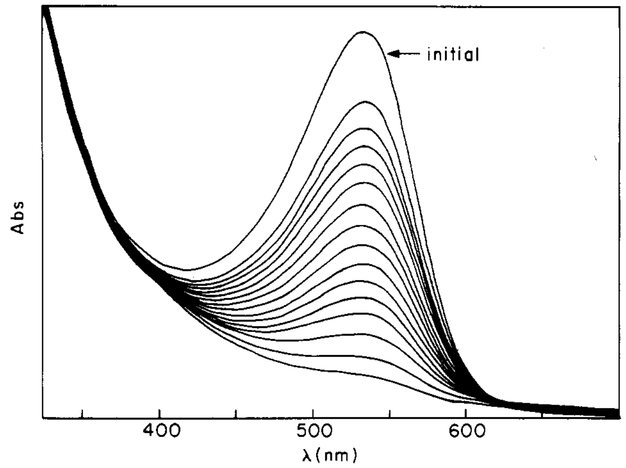

Figure 1. Spectrum of $(PPN)_2[Ir_8(CO)_{22}]$ (6.2×10^{-5} M) in methylene chloride under N_2 and successive spectra recorded periodically during photolysis at 520 nm.

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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[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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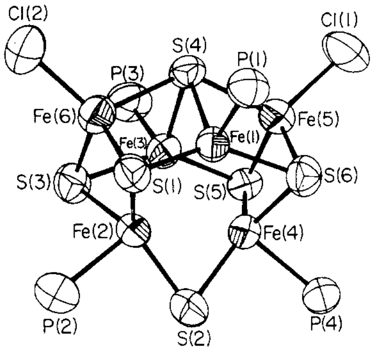

Figure 1. Structure of $[Fe_6S_6(P(n\text{-}Bu)_3)_4Cl_2]$ (C atoms omitted) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Ranges or individual values of interatomic distance (Å) and angle (deg) types related under idealized C_{2v} symmetry: Fe(1)–Fe(2), 2.670–2.702; Fe(1)–Fe(6), 2.643–2.679; Fe(2)–Fe(6), 2.689, 2.696; Fe(1)–Fe(3), 2.835; Fe (2)–Fe(4), 2.655 (7); Fe(1)–S(1), 2.177–2.197; Fe(2)–S(1), 2.203–2.233; Fe(6)–S(1), 2.241–2.281; Fe(2)–S(2), 2.154, 2.182; Fe(1)–S(4), 2.203, 2.215; Fe(6)–S(4), 2.331, 2.345; Fe(6)–Cl(2), 2.186, 2.200; Fe(1)–P(1), 2.289, 2.316; Fe(2)–P(2), 2.324, 2.306; Fe(2)–S(2)–Fe(4), 75.5; S(1)–Fe(1)–S(6), 137.9, 138.7; Fe(1)–S(4)–Fe(6), 71.0–71.9; Fe(5)–S(4)–Fe(6), 130.6; Fe(1)–S(4)–Fe(3), 79.8; Fe–μ_3-S–Fe, 72.8–75.8. Esd's for Fe–Fe distances, Fe–S distances, and all angles are 0.005–0.007 Å, 0.010–0.012 Å, and 0.3–0.4°, respectively.

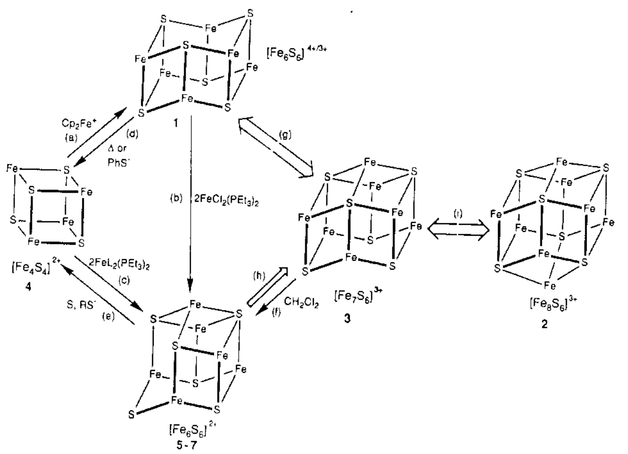

Figure 2. Core conversion reactions of iron–sulfur clusters. Solid arrows: experimental conversions a–e; open arrows: topological relationships. Reactions a[1b] and d[1a,c,e] have been reported earlier; reactions b, c (L = X^-, PhS^-), e, and f were observed in this investigation.

Reaction of a suspension of $(n\text{-}Bu_4N)_2[Fe_4S_4Cl_4]$[11] (**4**; 1.0 mmol) and $[Fe(PEt_3)_2Cl_2]$[12] (2.0 mmol) in 20 mL of acetonitrile followed by recrystallization of the product from dichloromethane/hexanes afforded black crystalline $[Fe_6S_6(PEt_3)_4Cl_2]$ (**5**; 70%).[13,14] Similarly, the reaction system $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$[15] (**4**; 4.6 mmol) + $[Fe(PEt_3)_2(SPh)_2]$[13] (9.2 mmol) in acetonitrile (20 mL; 50 °C, 6 h) gave, after workup from THF/hexanes, black crystalline $[Fe_6S_6(PEt_3)_4(SPh)_2]$ (**6**; 65%).[14] Further, cluster **5** (70%) was obtained from the reaction of a suspension of $(Et_4N)_3[Fe_6S_6Cl_6]$[1a–c] (**1**; 0.22 mmol) and $[Fe(PEt_3)_2Cl_2]$ (0.44 mmol) in acetonitrile (10 mL) followed by recrystallization (CH_2Cl_2/ether) of the crude product. These clusters are also readily accessible from self-assembly reactions: equimolar $[Fe(PEt_3)_2Cl_2]$ or $[Fe(PEt_3)_2(SPh)_2]$ (5.3 mmol) + $(Me_3Si)_2S$ in THF (80 mL; 12 h, followed by solvent removal and recrystallization from CH_2Cl_2 (**5**) or THF (**6**) and hexanes) affords **5** (64%) or **6** (70%). Also prepared by one or more of these procedures were $[Fe_6S_6(PEt_3)_4X_2]$ (X = Br^-, I^-), $[Fe_6S_6(P\text{-}n\text{-}Bu_3)_4Cl_2]$ (**7**), and $[Fe_6Se_6(PEt_3)_4Cl_2]$. Single crystals of **7** were obtained by diffusion of acetonitrile into a THF solution.

The structure of the $Fe_6S_6P_4Cl_2$ portion of **7**,[13] displayed in Figure 1, contains three types of bridging sulfur atoms[16] and provides the first instance of an iron–sulfur cluster not built *entirely* from Fe_2S_2 rhombs. The $[Fe_6(\mu_2\text{-}S)(\mu_3\text{-}S)_4(\mu_4\text{-}S)]^{2+}$ core is constructed from six such rhombs to form a basket with atoms Fe(2), Fe(4), and S(2) serving as the handle. It approaches idealized C_{2v} symmetry, with the C_2 axis passing through S(2,4). All Fe–Fe distances are within bonding range; the weakest interaction is Fe(1)···Fe(3) (2.835 (5) Å). The stereochemistry at chloride sites Fe(5,6) is approximately tetrahedral, but that at phosphine sites Fe(1–4) is more nearly planar pyramidal. Iron atom displacements toward phosphorus atoms above the S_3 planes are ≤0.14 Å, the mean P–Fe–S angle is 93.3°, and the μ_3-S–Fe(1,3)–μ_3-S angles are exceptionally large (mean 138.3°). Similar coordination sites occur in **3** and $[Co_7S_6(PPh_3)_5Cl_2]$,[10] suggesting this to be an inherent stereochemical component of phosphine-substituted $Fe_{6,7}S_6$ cores. The site pattern of the terminal ligands corresponds to that isomer with the minimal phosphine–phosphine interactions of the three possible isomers of C_{2v} symmetry. Cluster **6** was shown to have the same core structure, but poor crystal quality has thus far precluded precise determination of metric features.

Clusters **5** and **6** exhibit delocalized, spin-coupled structures but with different ground spin states in the crystalline phase. The susceptibility of **5** follows $\chi_M = 0.993/(T + 4.49)$ at 6.0–200 K with μ_{eff} = 2.83 μ_B corresponding to S = 1, whereas **6** is diamagnetic. However, in solution both achieve the triplet spin state (2.90 (**5**) and 2.88 μ_B (**6**), $CDCl_3$, 298 K), as do the other clusters $[Fe_6S_6(PEt_3)_4X_2]$. The appearance of two equally intense, isotropically shifted ethyl group resonances in the ^1H NMR spectra[14] of **5** and **6** is consistent with retention of core C_{2v} structure in solution.[17]

Clusters **1**–**7** form a set whose cores may be interconverted in an actual or a formal topological sense, as represented in Figure 2. Experimental conversions in the form of oxidative process a and the reduction c are the only known enlargement transformations of the $[Fe_4S_4]^{2+}$ core, itself a thermodynamic sink in many cluster formation reactions. These conversions occur in about 70% to near-quantitative yields. Inspection of the structure of **7** readily shows that the basket contains four of the six fused Fe_2S_2 rhombs of the prismane core. Reaction b results in a one-electron reduction of the $[Fe_6S_6]^{3+}$ core and phosphine substitution for chloride, whose effect is isomerization of the D_{3d} prismane core to the C_{2v} form. Operationally, this requires rupture of a vertical Fe–S core bond in **1**, movement of Fe(1) inward toward S(4) (Figure 1), and

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(13) Experimental data: All reactions and manipulations were performed under anaerobic conditions. $[Fe(PEt_3)_2(SPh)_2]$ was formed in situ in acetonitrile or THF by the reaction of stoichiometric amounts of $FeCl_2$, NaSPh, and PEt_3; NaCl was removed by filtration. X-ray diffraction data were collected as previously performed[9] with use of graphite-monochromatized Mo Kα radiation. Compound **7** crystallized in the tetragonal space group $I4_1$ with a = 33.78(1) Å, c = 12.362(7) Å, and Z = 8. From 4687 total reflections the structure of **7** was solved from 2396 unique data ($3 \leq 2\theta \leq 45°$, $I \geq 1.8\sigma(I)$) by a combination of direct methods (MULTAN) and Fourier techniques (CRYSTALS). Refinement with all but carbon atoms described anisotropically converged at R (R_w) = 9.50 (7.65)%. The n-butyl groups were found to possess large thermal parameters, indicative of disorder. A final difference Fourier map revealed 10 peaks with heights of 0.5–0.8 e/Å^3, all located within bonding distance of the organic groups. This disorder was left untreated due to limitations in the number of data. The core structure is, however, well defined. Compound **6** crystallized in space group $P2_1/a$ with a = 21.27 (1) Å, b = 10.428 (3) Å, c = 24.39 (1) Å, β = 96.20 (4)°, and Z = 4.

(14) All new compounds gave satisfactory elemental analyses. λ_{max} (ϵ_M): 320 (sh, 27 300) nm (**5**, CH_2Cl_2); 298 (sh, 34 800) nm (**6**, THF). ^1H NMR ($CDCl_3$, 297 K): δ 0.14 (CH_3), –0.15 (CH_3), –6.59 (CH_2), –7.72 (CH_2) (**5**); δ 11.7 (2, *o*-H), 11.5 (1, *p*-H), 4.14 (2, *m*-H), 0.22 (CH_3), –0.25 (CH_3), –5.15 (CH_2), –5.70 (CH_2) (**6**).

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(17) The two prismane isomers $Fe_6S_6L_4L'_2$ would also exhibit pairwise inequivalence of L ligands.

formation of the Fe(1)–S(4) bond with concomitant core metric changes. The prismane clusters **1** (L = X^-, RO^-, RS^-) exhibit in cyclic voltammetry a quasi-reversible 3–/4– electron-transfer step implicating a chemically unstable reduced cluster.[1c,e] It remains to be learned if the 4– cluster, isoelectronic with **5–7**, undergoes core isomerization or whether tertiary phosphine is obligatory to the stability of this form of $[Fe_6S_6]^{2+}$, presumably by inducing planar-pyramidal FeS_3P coordination sites. It is these sites, present in the two open (nonrhomboidal) Fe_3S_3 faces of the core, that appear to impart stability to the C_{2v} arrangement. Conversions d and e reduce core nuclearity, and reaction f is the spontaneous degradation of **3** in solution to the far more stable cluster **5**.

The remaining transformations in Figure 2 are of a formal topological nature, so described because they have not been effected experimentally. Thus, the capping reactions g and h generate the $[Fe_7S_6]$ core of **3**. This is the topological link between the D_{3d} and C_{2v} forms of the $[Fe_6S_6]$ core and the cuboctahedral $[Fe_8S_6]$ core of **2**, derived here by capping reaction i. We note these formal relationships in addition to demonstrated conversions in order to draw attention to the conceivable development of a rational cluster synthesis and conversion chemistry spanning the limits $[Fe_2S_2]$ to $[Fe_8S_6]$. Indeed, certain conversions among smaller cores, viz., $[Fe_2S_2]^{2+} \rightarrow [Fe_4S_4]^{2+}$,[18] $[Fe_2S_2]^{+} \rightarrow [Fe_4S_4]^{2+}$,[18] linear $[Fe_3S_4]^{+} \rightarrow [Fe_4S_4]^{2+}$,[16b] and cuboidal $[Fe_3S_4]^{0} \rightarrow [Fe_4S_4]^{2+}$ [19] (with protein clusters), have already been accomplished. Subsequent reports will provide more detailed descriptions of **5–7** and related clusters and their reactivities, including core conversions.

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Supplementary Material Available: Tables of atom positional and thermal parameters for $[Fe_6S_6(P(n\text{-}Bu)_3)_4Cl_2]$ (3 pages). Ordering information is given on any current masthead page.

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Pulse Radiolysis Studies of Berkelium(III): Preparation and Identification of Berkelium(II) in Aqueous Perchlorate Media[1]

Sir:

The chemistry of the transplutonium elements in aqueous solutions has been predominantly concerned with the interactions of the trivalent cations and complexing ligands.[2] Quasi-thermodynamic arguments have been advanced to predict that the +2 and +4 oxidation states of these elements would respectively be very powerful reductants and oxidants.[3] Previous pulse radiolysis investigations in this laboratory have provided evidence for the existence of divalent oxidation states of Am, Cm, and Cf as transient species[4] in aqueous noncomplexing media with the hydrated electron as the reducing agent. There have been a number of elegant solid-state studies that have provided indirect evidence for the existence of Bk(II),[5] but the results obtained in the present investigation provide the first direct evidence for the existence of this oxidation state in aqueous media.

Earlier efforts to search for Bk(II) by pulse radiolysis were hampered by the necessity for relatively high pH for two reasons: (1) a buffer solution cannot be used, so pH adjustment and control are difficult, and (2) aqueous Bk(III) is spontaneously oxidized to Bk(IV) by atmospheric oxygen at relatively high pH since the Bk(IV) hydrolyzes rapidly and precipitates as a hydrous dioxide even at pH 5. These barriers were surmounted by the use of bicarbonate to adjust pH, by maintaining rigorously oxygen free conditions, and by using ethanol to suppress radiolysis products.

Experimental Section. Sodium bicarbonate, perchloric acid, and ethanol stock solutions were prepared from analytical grade reagents and standardized by conventional techniques. The ^{249}Bk ($t_{1/2}$ = 320 days) was purified from its daughter, ^{249}Cf, by a solvent extraction technique[6] prior to the pulse radiolysis experiments. The purified Bk in a nitric acid–peroxide solution was evaporated to dryness; the Bk was redissolved in 10^{-3} M perchloric acid and fumed to dryness. This procedure was repeated, and the berkelium(III) perchlorate salt was dissolved in an aqueous solution containing 0.1 M ethanol to scavenge $OH^{\bullet}$ produced by radioactive decay. The pH was adjusted to 5 by the addition of a solution of 0.1 M sodium bicarbonate–0.1 M ethanol under an atmosphere of Ar.

The rate of disappearance of the hydrated electron was monitored at 600 nm by using the photomultiplier pulse radiolysis technique.[7] The Argonne streak camera system[8] was used to obtain the spectrum of the Bk(II).

Results and Discussion. The freshly prepared solution (2.0×10^{-3} M in Bk(III), pH 5, 0.1 M ethanol, Ar saturated) was irradiated with a 4-ns pulse of electrons (ca. 0.7 krad), and from the photomultiplier signal, the resultant first-order rate of decay of the hydrated electron was calculated to be $2.25 \times 10^6\ s^{-1}$, with the concomitant second-order rate constant of $1.12 \times 10^9\ M^{-1}\ s^{-1} \pm 2.5\%$. This value is to be compared to $1.6 \times 10^8\ M^{-1}\ s^{-1}$ for the reduction of Am(III) and $3 \times 10^9\ M^{-1}\ s^{-1}$ for that of Cf(III), by the hydrated electron. The estimated values of the +3/+2 couples are respectively –2.3, –2.8, and –1.6 V for Am, Bk, and Cf. The ordering of log k vs $E°$ is not linear. A comparison with the values that have previously been obtained for the reduction of the 4f transition elements also presents no readily discernible reactivity pattern based on either potential values or electronic structure.[9]

This result led to an attempt to provide direct evidence for the preparation of Bk(II). A Bk(III) solution of the same composition as above was irradiated with a 40-ns pulse of electrons (ca. 5 krad), and a time-resolved absorption spectrum was observed with the streak camera system, with a maximum at about 310 nm. The three-dimensional spectrum is displayed in Figure 1. Because of the experimental constraints on solution composition, the principal reactive radical is the hydrated electron. The observed transient grows in with the same halflife with which that species disappears, i.e. about 0.3 μs. The absorption is therefore believed

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