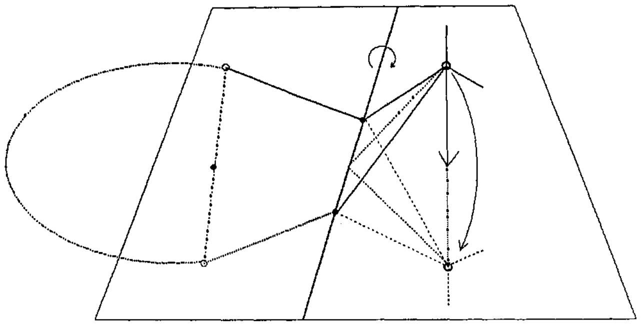

Figure 1. Illustration of corner flapping process for transforming a ring conformer. Circled atom at top right is the corner to be flapped. Two α ring atoms (solid circles) and the midpoint (solid circle) of two β ring atoms (open circles) define a plane. The corner atom is moved across the plane to the opposite side.

Table I. Performance of Corner Flapping in Generating Energy Minimum Conformations of Lower Cycloalkanes C_nH_{2n} (n = 6–14)

n	time,[a] h	N[b]
6	0.13	2 (2)
7	0.17	2 (2)
8	0.44	4 (4)
9	0.86	5 (5)
10	3.80	14 (15)
11	12.47	15 (27)
12	1.31[c]	18 (87)
13	2.24[c]	44 (116)
14	3.47[c]	44 (159)

[a] Unless otherwise noted, time is measured on a VAX Station 2000 under the single-task mode. [b] Number of conformers having Boltzmann distributions larger than 0.01%. Parenthesized is the total number of conformers generated by the corner flapping calculation. [c] Time measured on a mainframe computer (HITAC M-682).

flapping the corner atom to below the plane produces a different conformer, as we often practice with the framework molecular model. In order to program the flapping process, it is convenient to define a local plane based on several ring atoms near the corner and displace the corner atom vertically to the mirrored position on the other side of plane (Figure 1).

The flapping process is equivalent to simultaneously rotating, in disrotatory fashion, two endocyclic bonds extending from the corner atom. The new conformation thus obtained is optimized with any computational method like MM2[4] and compared with the saved conformers by conventional criteria including steric energy, dihedral angle pattern, and symmetry considerations. A structure is saved only when a new conformer is obtained, but otherwise discarded. When all the corners have been flapped, this structure is marked as *finished*. Thereupon, the most stable of the *unfinished*, saved conformers is subjected to the next flapping/minimization process. It should be noted that this algorithm does not produce a tree structure as in the other systematic algorithms, since every branch is immediately pruned to retain only the new conformer. The search terminates when all the saved conformers have been flagged as *finished*.[5]

Cycloalkanes up to a 14-membered ring were first tested (Table I). The total number of conformers and the structural details of the conformers found agree with those described by the stochastic search method.[1c] For cyclic molecules having rotatable side chains, one might assume that the attachment of side chains in all possible rotationally isomeric conformations to every possible ring conformer should produce all possible structures. The assumption is, however, unsafe in view of the recently recognized conformational coupling phenomenon.[6] Our algorithm is hence combined with the exhaustive rotation of the side chain.[2a] The program has been successfully tested for several substituted cyclohexanes.[7]

Two features of the corner flapping algorithm must be responsible for its high speed as shown in Table I. First, the flapping operation never fails to cross over the barrier separating different conformers, hence the new conformation does not return to the original one during subsequent energy minimization. Secondly, the structure is perturbed by the flapping operation only in the immediate vicinity of the corner, and the new conformation that resulted can quickly adjust itself to a new energy minimum.[8]

Acknowledgment. We thank Professor M. Saunders for valuable information and the Ministry of Education for financial support through Grants-in-Aid for Scientific Research No. 63470011 and 63607501.

Supplementary Material Available: Table of MM2-optimized Cartesian coordinates (carbon atoms only) and steric energies of all conformers listed in Table I (41 pages). Ordering information is given on any current masthead page.

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(4) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC 1982.

(5) During the whole search, the process of flapping of all corners is repeated N times, where N is the total number of conformers for the ring compound in question. If the average time of each geometry optimization is t seconds, and the number of corners in the molecule n, the computer time necessary to terminate the search is approximately equal to nNt seconds. When MM2 is used, t is 90 s for cyclodecane on VAX Station 2000. N is generally unknown, but the parenthesized N in Table I should provide some measure.

(6) Iratcabal, P.: Liotard, D. *J. Am. Chem. Soc.* **1988**, *110*, 4919.

(7) Program CONFLEX2 has been submitted to QCPE.

(8) A referee questioned the validity of our fundamental assumption that there will not be any other networks of conformers that are not connected to the one found through single flaps. We have at the moment no proof for this assumption, but our test calculations have so far reproduced all those found by random methods. As a further check, we began testing *double flaps*, wherein all pair-wise combinations of corners are flapped, and still have not found any new conformers other than those found by single flaps.

A High-Intensity Molecular Beam of Vinyl and Ethynyl Radicals

Joel A. Blush, Jeunghee Park, and Peter Chen*[†]

Mallinckrodt Chemical Laboratory, Harvard University
Cambridge, Massachusetts 02138

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We report a clean, high-yield, high-number-density ($>10^{14}$ cm^{-1} at the nozzle) source of vinyl (**1**) and ethynyl (**2**) radicals for gas-phase spectroscopic investigations. Supersonic jet flash pyrolysis[1] of *tert*-butyl peracrylate (**3**) and *tert*-butyl perpropriolate (**4**), seeded in a continuous helium expansion, gives near-quantitative conversion to radical products. Products and yields were probed by 10.49-eV vacuum UV laser photoionization mass spectroscopy.[2] Loss of radicals by bimolecular reactions amounted to no more than ≈20% of the nascent species. We hope to exploit the unique features of supersonic pyrolysis jets as a gas-phase analogue to cryogenic matrix isolation for the spectroscopy and energetics of organic reactive intermediates.

tert-Butyl peresters were prepared in ≈40% (for **3**) and 80% (for **4**) yield via the acid chlorides by a low-temperature Schotten–Baumen procedure.[3] Attempted carbonyldiimidazole and ethyl[3-(dimethylamino)propyl]carbodiimide (EDC) mediated couplings[3] of acrylic or propriolic acid with t-BuOOH were unsuccessful. Propriolyl chloride[4] was prepared by slow addition

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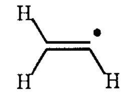
[†] NSF Presidential Young Investigator, David and Lucile Packard Fellow, Shell Faculty Fellow, Camille and Henry Dreyfus Distinguished New Faculty Fellow.

(1) Chen, P.; Colson, S. D.; Chupka, W. A.; Berson, J. A. *J. Phys. Chem.* **1986**, *90*, 2319.

(2) Chen, P.; Colson, S. D.; Chupka, W. A. *Chem. Phys. Lett.* **1988**, *147*, 466.

(3) For a review of perester syntheses and reactions, see: Singer, L. A. In *Organic Peroxides*; Swern, D., Ed.; John Wiley: New York, 1970; Vol. 1.



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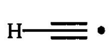

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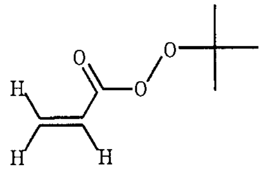

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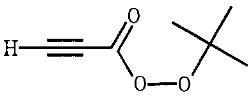

4

of proprilic acid to PCl_5 and distilled at room temperature under reduced pressure. Slow addition of the acid chloride to a cooled (−78 °C) CH_2Cl_2 solution of the hydroperoxide was followed by slow, dropwise addition of pyridine. After stirring for 1 h, the pyridinium chloride precipitate was removed by filtration. Repeated extraction of the CH_2Cl_2 perester solution with aqueous base, followed by further purification by careful distillation under reduced pressure ($T \leq 35$ °C, ≈2 Torr), resulted in better than 95% pure perester, as indicated by NMR. The purified peresters are colorless liquids at room temperature with a characteristic odor. NMR and IR spectra[5] are in satisfactory agreement with the proposed structure.

tert-Butyl peresters were chosen, on the basis of the extensive solution-phase studies of their thermal decomposition.[3] In particular, percinnamates[6] and perphenylpropriolates[7] are reported to cleave to the phenyl-substituted vinyl and ethynyl radicals by decarboxylation of the corresponding acyloxy radicals. Time-resolved ESR studies[8] of benzoyloxy radicals measured $E_a = 5.8$ kcal/mol for decarboxylation, suggesting that, under pyrolytic conditions, rate-determining cleavage of a perester O–O bond is rapidly followed by loss of CO_2. One therefore expects peracrylate **3** and perpropriolate **4** to give C_2H_3 and C_2H, CO_2, CH_3, and acetone (the latter two from *tert*-butoxy radical). Time-of-flight mass spectra of the peresters were taken to assess their efficacy as gas-phase radical precursors. A partial pressure of <0.3 Torr of the perester was seeded into 0.4 atm of helium and expanded through a resistively heated 600-μm-i.d. Al_2O_3 pyrolysis tube nozzle. After skimming, the molecular beam was crossed by the photoionization laser. Electron-impact ionization was judged unsuitable on the basis of extensive fragmentation of the parent ion to give $C_2H_n^+$ species (Kratos MS-50, direct insertion probe, 7–70 eV). Radiation for photoionization (118.2 nm, 10.49 eV) was generated by frequency-tripling the Nd:YAG third harmonic in xenon.[2] Figure 1 shows the time-of-flight mass spectra for *tert*-butyl peracrylate with and without pyrolysis. As is evident by the observed peaks, the ≈1500-K, 50-μs pyrolysis results in the high conversion of perester into products. Mass spectra from the perpropriolate are similar. From the mass spectra, we conclude the following:

(1) Photoionization of the unpyrolyzed perester gives a parent ion that primarily cracks to give *tert*-butyl cation ($m/e = 57$). Small peaks correspond to cleavage α or β to the carbonyl. Most significantly, vacuum UV photoionization is a gentle detection method that gives no low-mass fragments.

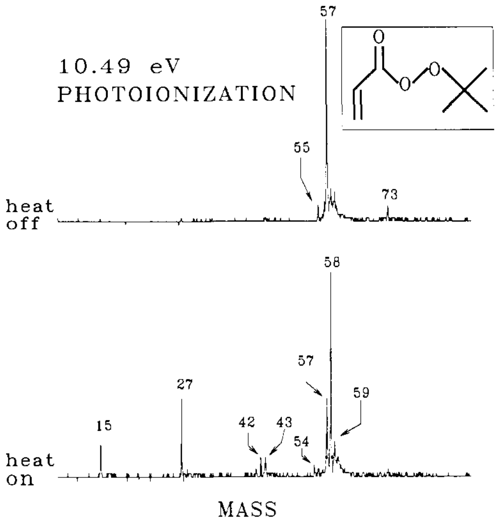

Figure 1. Time-of-flight mass spectra of *tert*-butyl peracrylate with and without pyrolysis. Methyl radical ($m/e = 15$), vinyl radical ($m/e = 27$), and acetone ($m/e = 58$) are the primary pyrolysis products. Radical–radical recombination products at $m/e = 42$ and 54 are small in comparison.

(2) Perester flash pyrolysis is exceptionally clean. Pyrolytic cleavage of the peroxide O–O bond gives *tert*-butoxy and acyloxy radicals, which cleave cleanly to CH_3 ($m/e = 15$), acetone ($m/e = 58$), CO_2 ($m/e = 44$), and vinyl or ethynyl ($m/e = 27$, 25). All of these predicted primary radical and stable products with ionization potentials below 10.49 eV are observed. IP(CO_2) is too high. All other observed peaks are small in comparison. IP(C_2H), reported[9] to be ≈11.6 eV, precludes direct observation of ethynyl at 118 nm. However, clean production of CH_3 and acetone suggests that, just as peracrylate **3** gives vinyl radical **1**, perpropriolate **4** produces ethynyl radical **2**.

(3) Because the relative photoionization cross section of vinyl versus methyl radical is unknown, there is no simple determination of number density from mass spectral peak heights. Neither radical, however, can disappear at greater than the gas-kinetic rate, so one would expect comparable numbers of the two species.

(4) Small peaks in the pyrolyzed peracrylate spectrum at $m/e = 42$ and 54 are assigned to propene and 1,3-butadiene, respectively. The presence of these radical–radical recombination products supports the contention that methyl and vinyl radicals were produced in the pyrolysis. The corresponding peaks at $m/e = 40$ and 50 in the perpropriolate spectrum are assigned to analogously produced propyne and diacetylene. The small relative size of these peaks indicates that bimolecular loss processes for the radicals have been successfully minimized in the supersonic jet flash pyrolysis technique.

(5) Radical-induced decomposition of the unsaturated peresters occurs by attack of methyl radical at the carbon–carbon multiple bond, as in the radical-induced decomposition of benzoyl peroxide.[10] Loss of CO_2 or CO from an intermediate α-lactone gives small peaks at $m/e = 40$ and 56, respectively, in the mass spectrum of pyrolyzed perpropriolate. Suppression of these peaks upon further dilution of the perester in helium is consistent with their bimolecular origin. Analogous mass peaks from the peracrylate are indistinguishable from the unimolecular reaction products. The small $m/e = 72$ peak in the pyrolyzed perpropiolate is assigned to C_4H_8O, produced by pyrolytic syn elimination of 2-methoxypropene from the Criegee rearrangement[3] product of *tert*-butyl perpropriolate.

Supersonic jet flash pyrolysis of peresters is a convenient, general route to even the hard-to-make unsaturated σ-radicals. We have demonstrated the ease and versatility of the method as a clean source of vinyl and ethynyl radicals. Studies relating to the

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(4) Balfour, W. J.; Greig, C. C.; Visaisouk, S. *J. Org. Chem.* **1974**, *39*, 725.

(5) **3**: NMR δ 1.33 (s, 9 H), 5.89 (dd, 10.5 Hz, 1.5 Hz, 1 H), 6.10 (dd, 17 Hz, 10.5 Hz, 1 H), 6.47 (dd, 17 Hz, 1.5 Hz, 1 H); IR 1770, 1640, 1120 cm^{-1}. **4**: NMR δ 1.33 (s, 9 H), 3.03 (s, 1 H); IR 2110, 1760, 1140 cm^{-1}.

(6) Bartlett, P. D.; Hiatt, R. R. *J. Am. Chem. Soc.* **1958**, *80*, 1398. Kampmeier, J. A.; Fantazier, R. M. *J. Am. Chem. Soc.* **1966**, *88*, 1959. Singer, L. A.; Kong, N. P. *J. Am. Chem. Soc.* **1966**, *88*, 5213; **1967**, *89*, 5251.

(7) Traylor, T. G.; Sieber, A.; Kiefer, H.-R.; Clinton, N. *Intra-Sci. Chem. Rep.* **1969**, *3*, 289.

(8) Yamauchi, S.; Hirota, N.; Takahari, S.; Misawa, H.; Sawabe, K.; Sakuragi, H.; Tokumaru, K. *J. Am. Chem. Soc.* **1989**, *111*, 4402.

(9) Wyatt, J. R.; Stafford, F. E. *J. Phys. Chem.* **1972**, *76*, 1913.

(10) Walling, C.; Savas, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 1738. Walling, C.; Cekovic, Z. *J. Am. Chem. Soc.* **1967**, *89*, 6681.

spectroscopy and thermochemistry of these species are underway.

Acknowledgment. We acknowledge contributions from D. W. Kohn and H. Clauberg, who constructed the spectrometer used in this work, and Lin Chu, who worked on the perester syntheses. Funding for the lasers used in this work by the National Science Foundation is also acknowledged.

New Mo–Fe–S Clusters via Oxidative Decarbonylation Reactions: The $[MoFe_5S_6(CO)_6L_3]^{n-}$ (L = PEt_3, n = 0; L = I, n = 2) Capped Cubanes

K. S. Bose,[1a] S. A. Chmielewski,[1a] P. A. Eldredge,[1b]
E. Sinn,[1a] and B. A. Averill*,[1a]

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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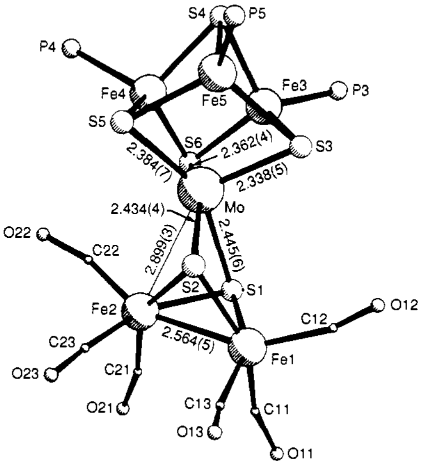
We have recently reported[2,3] a novel approach to the synthesis of Mo–Fe–S clusters as models for the iron-molybdenum cofactor (FeMo-co)[4] of nitrogenase, a small dissociable cluster of approximate stoichiometry[4,5] $MoFe_{6-7}S_{8-10}$ and as yet unknown structure that appears to constitute the site at which dinitrogen is reduced by the enzyme.[6] Our approach differs from other attempts to produce synthetic models[7,8] of FeMo-co in that the Mo–S–Fe unit(s) are formed by reaction of the $[Fe_2S_2(CO)_6]^{2-}$ ion[9] with various molybdenum sources; it has been the first to produce high-nuclearity clusters with >4Fe/Mo that approximate the core composition and Mo–Fe distance distribution of FeMo-co, e.g., the $[MoFe_6S_6(CO)_{16}]^{2-}$ ion (I).[2] Articulation of clusters such as I into more accurate structural models for FeMo-co requires the development of methodology for oxidative decarbonylation with preservation of the high-nuclearity nature of the cluster. We report herein initial results indicating that such reactions can be effected and that they produce Mo–Fe–S clusters with unusual and potentially relevant structures.



Mo-Fe3	2.655(3)	Fe3-Fe4	2.607(5)
Mo-Fe4	2.668(3)	Fe4-Fe5	2.605(4)
Mo-Fe5	2.677(3)	Fe3-Fe5	2.611(5)

Figure 1. PLUTO drawing of the $MoFe_5S_6(CO)_6(PEt_3)_3$ cluster, showing the atomic numbering scheme and selected interatomic distances. The ethyl groups on the PEt_3 ligands have been omitted for clarity.

Reaction of the Et_4N^+ salt of I[2] with 2 equiv of I_2 in THF at room temperature results in evolution of CO and formation of a dark brown solution. Removal of THF in vacuo, followed by dissolution in a minimal amount of MeCN, filtration, addition of Et_2O, and cooling to −20 °C overnight, produces $(Et_4N)_2[MoFe_5S_6(CO)_6I_3]$ (II) in virtually quantitative yield.[10] Although X-ray quality crystals of II have not yet been obtained, its identity is inferred by comparison to the phosphine derivative $MoFe_5S_6(CO)_6(PEt_3)_3$ (III), which precipitates as microcrystals in 50–60% yield upon addition of 3 equiv of PEt_3 to a solution of II in MeCN at room temperature.[11] The identity of III has been established by a single-crystal X-ray diffraction study,[12] which together with spectroscopic and magnetic studies demonstrates the existence of novel "capped-cubane" clusters containing the $[MoFe_5S_6(CO)_6]^{0,+}$ cores in III and II, respectively.

The structure of cluster III (Figure 1) consists of an $MoFe_3S_4$ cubane "capped" by an $Fe_2S_2(CO)_6$ unit to produce the $MoFe_5S_6(CO)_6$ core stoichiometry. Notable features of the structure include the following. (i) One Fe atom of I has been lost during the reaction, with retention of all six S atoms. (ii) An Fe–Mo bonding interaction is observed in the $MoS_2Fe_2(CO)_6$ unit: the Mo–Fe(2) distance is 2.899 (3) Å vs 3.614 (3) Å for Mo–Fe(1). This is compensated for by an increase of ca. 0.1 Å in the Fe(1)–Fe(2) distance vs the parent $Fe_2S_2(CO)_6$. Such a bonding interaction between the central metal and one of the Fe atoms of "a discrete $Fe_2S_2(CO)_6^{2-}$ unit" has not been previously ob-

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[1] (a) University of Virginia. (b) University of North Carolina.

[2] Eldredge, P. A.; Bryan, R. F.; Sinn, E.; Averill, B. A. *J. Am. Chem. Soc.* **1988**, *110*, 5573.

[3] Bose, K. S.; Lamberty, P. E.; Kovacs, J. A.; Sinn, E.; Averill, B. A. *Polyhedron* **1986**, *5*, 393.

[4] Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249.

[5] (a) Burgess, B. K.; Jacobs, D. R.; Stiefel, E. I. *Biochem. Biophys. Acta* **1980**, *614*, 196. (b) Yang, S.-S.; Pan, W.-H.; Friesen, G. D.; Burgess, B. K.; Corbin, J. L.; Stiefel, E. I.; Newton, W. E. *J. Biol. Chem.* **1982**, *257*, 8042. (c) Nelson, M. J.; Levy, M. A.; Orme-Johnson, W. H. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 147. (d) Stiefel, E. I.; Cramer, S. P. In *Molybdenum Enzymes*; Spiro, T., Ed.; Wiley-Interscience: New York, 1985; p 89.

[6] (a) Burgess, B. K. In *Advances in Nitrogen Fixation Research*; Veeger, C., Newton, W. E., Eds.; Nijhoff-Junk-Pudoc: Dordrecht, 1983; p 103. (b) Nelson, M. J.; Lindahl, P. A.; Orme-Johnson, W. H. In *Advances in Inorganic Biochemistry*; Eichhorn, G., Marzilli, L., Eds.; Plenum Press: 1982; Vol. 4, pp 1–40. (c) Burgess, B. K.; Newton, W. E. In *Nitrogen Fixation, The Chemical-Biochemical-Genetic Interface*; Müller, A., Newton, W. E., Eds.; Plenum Press: New York, 1983; p 83. (d) Burgess, B. K. In *Nitrogen Fixation Research Progress*; Evans, H. J., Bottomley, P. J., Newton, W. E., Eds.; Martinus Nijhoff Publishers: Dordrecht, 1985; p 543. (e) Burgess, B. K. In *Molybdenum Enzymes*; Spiro, T., Ed.; Wiley-Interscience: New York, 1985; p 161.

[7] (a) Holm, R. H.; Simhon, E. D. In *Molybdenum Enzymes*; Spiro, T., Ed.; Wiley-Interscience: New York, 1985; p 1. (b) Averill, B. A. *Struct. Bonding (Berlin)* **1983**, *53*, 59. (c) Coucouvanis, D. In *Nitrogen Fixation, The Chemical-Biochemical-Genetic Interface*; Müller, A., Newton, W. E., Eds.; Plenum Press: New York, 1983; p 211. (d) Garner, C. D.; Acott, S. R.; Christou, G.; Collison, D.; Mabbs, F. E.; Petrouleas, V.; Pickett, C. J. In *Nitrogen Fixation, The Chemical-Biochemical-Genetic Interface*; Müller, A., Newton, W. E., Eds.; Plenum Press: New York, 1983; p 245. (e) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201.

[8] (a) Coucouvanis, D.; Salifoglou, A.; Kanatzidis, M. G.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1987**, *109*, 3807. (b) Salifoglou, A.; Kanatzidis, M. G.; Coucouvanis, D. *J. Chem. Soc., Chem. Commun.* **1986**, 559. (c) Kanatzidis, M. G.; Coucouvanis, D. *J. Am. Chem. Soc.* **1986**, *108*, 337. (d) Coucouvanis, D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 5005. (e) Coucouvanis, D.; Al-Ahmad, S.; Salifoglou, A.; Dunham, W. R.; Sands, R. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1353.

[9] Seyferth, D.; Henderson, R. S.; Song, L. C. *Organometallics* **1982**, *1*, 125.

[10] Anal. Calcd for $(Et_4N)_2[MoFe_5S_6(CO)_6I_3]$, $C_{22}H_{40}Fe_5I_3MoN_2O_6S_6$: C, 19.18; H, 2.91; Fe, 20.28; I, 27.65; Mo, 6.97; N, 2.03; S, 13.97. Found: C, 19.03; H, 3.01; Fe, 19.74; I, 27.06; Mo, 6.76; N, 1.98; S, 13.89.

[11] The extreme oxygen sensitivity of III made obtaining reproducible elemental analysis data extremely difficult; the following values are typical of the ≥4 analyses obtained. Anal. Calcd for $MoFe_5S_6(CO)_6(PEt_3)_3$, $C_{24}H_{45}Fe_5MoO_6P_3S_6$: C, 26.44; H, 4.16; Fe, 25.62; Mo, 8.80; P, 8.52; S, 17.65. Found: C, 26.91; H, 4.25; Fe, 23.49; Mo, 8.50; P, 7.24; S, 18.28.

[12] Crystals of III were obtained by addition of excess Et_3P to a filtered reaction mixture containing $(Et_4N)_2[MoFe_6S_6(CO)_{16}]$ (1 equiv), I_2 (2 equiv) and ca. 20 equiv of LiCl in MeCN, followed by cooling to −20 °C overnight. The compound is virtually insoluble in MeCN and was obtained in very low yields by this method. X-ray diffraction measurements were performed on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Data were collected by the θ–2θ technique over the range $1.0° \geq 2\theta \geq 50°$. A total of 2857 reflections with $I \geq 3\sigma(I)$ were used in the refinement. III crystallizes in the triclinic space group $P\bar{1}$, with a = 10.760 (3) Å, β = 11.726 (4) Å, c = 18.558 (5) Å, α = 80.80 (4)°, β = 85.42 (3)°, γ = 70.30 (4)°, V = 2175 (3) Å^3, and Z = 2. The structure was solved by using the direct-methods program MULTAN; least-squares refinement gave R = 4.7% and R_w = 6.2% with anisotropic thermal parameters for all non-hydrogen atoms.