

and so electron transfer to a transition metal appears unlikely. It is possible that the missing electron has been transferred to (b)sulfite in the solution formed as a result of dithionite oxidation. This would require the enzyme-bound FMNH₂/FMN_{SO} couple to have an unprecedentedly low E_m of less than -550 mV (NHE).¹⁸ It would also require a >100 mV decrease in the FMNH₂/FMN_{SO} E_m value when (6R)-6-F-EPSP binds since, in the absence of this substrate analogue, no FMN_{SO} (<2%) is detected by EPR (insert A, Figure 1) or UV/visible spectroscopy (data not shown).

The observation of the stoichiometric formation of a stable N-5 flavin radical upon binding (6R)-6-F-EPSP to chorismate synthase was unexpected, as this was clearly not the same intermediate previously detected spectrophotometrically with the natural substrate EPSP.¹⁰ However, a free radical could be a transient intermediate in the enzyme reaction with EPSP which does not accumulate when rapid removal of a hydrogen radical from C-6 is possible.¹⁹

Acknowledgment. M.N.R. and S.B. are grateful to the Science and Engineering Research Council and ICI Agrochemicals for support under the CASE awards scheme for postgraduate studies.

(18) Mayhew, S. G. *Eur. J. Biochem.* **1978**, *85*, 535-547. The potential of the solution of 450 μ M Na₂S₂O₄ and 200 μ M Na₂SO₃ (100 μ M impurity in the Na₂S₂O₄ and 100 μ M from the reduction of FMN) is calculated to be ca. -520 mV, and for >90% conversion to the semiquinone state, the E_m of the FMNH₂/FMN_{SO} couple must be at least 30 mV lower. The lowest reported value for a flavoprotein FMNH₂/FMN_{SO} is that of a flavodoxin from *Azotobacter chroococcum*, $E_m = -520$ mV; ref 16.

(19) A mechanism involving the initial removal of a hydrogen radical from C-6 of EPSP has previously been proposed: Bartlett, P. A.; McLaren, K. L.; Alberg, D. G.; Fassler, A.; Nyfeler, R.; Lahun, C. T.; Grissom, C. B. *Proceedings of the Society for Chemical Industry Pesticides Group Meeting, BPCP Monogr. Ser.* **1989**, *42*, 155-170.

An (η^2 -Tetrafluoroethylene)ruthenium Complex with a Metallacyclopropane Structure but with a Low Barrier to Propellor Rotation

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The nature of the transition metal-olefin bond has been the subject of significant experimental and theoretical work over the past four decades. Various levels of theory concur that the two-component interaction originally proposed by Dewar, Chatt, and Duncanson² (Figure 1) is still the best way of picturing this interaction.³ Within a continuum of possible combinations of these two interactions, an increase in the contribution of the metal-d to olefin- π^* backbonding component is thought to be responsible for increased pyramidalization at the bound carbon atoms, leading to a more metallacyclopropane structure. The activation barriers to propellor rotation of the olefin about the metal-olefin bond axis have also been the subject of considerable theoretical and experimental attention.^{3,4} The rhodium complex

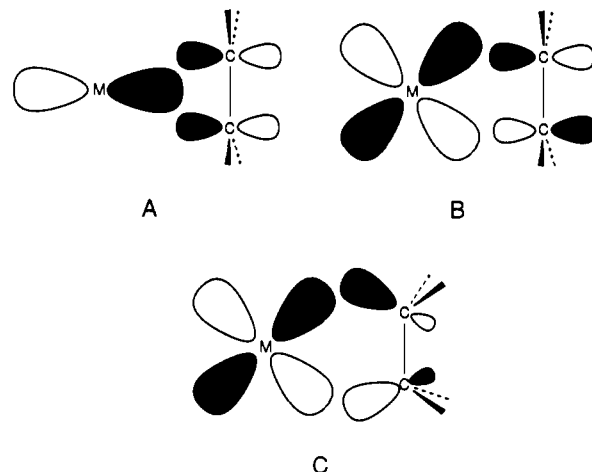


Figure 1. (A) The olefin-metal donor and (B) olefin-metal acceptor components of the olefin-metal bond. (C) Effect of pyramidalization at carbon on the acceptor component. See ref 3 for more comprehensive treatments.

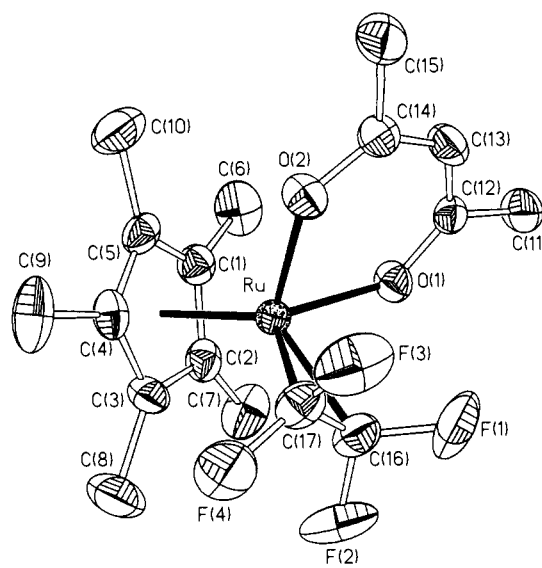


Figure 2. ORTEP representation of 3a.

1 is often used as a paradigm; its structure shows a more metallacyclopropane interaction for C₂F₄ than for C₂H₄. However, the C₂H₄ rotates fast on the NMR time scale yet the C₂F₄ is stereochemically rigid.^{5,6} Indeed, high barriers to propellor rotation are the norm for C₂F₄ complexes,^{7,8} and none has been

(5) (a) The structure of 1 is discussed in the following: Guggenberger, L. J.; Cramer, R. *J. Am. Chem. Soc.* **1972**, *94*, 3779. (b) NMR studies are discussed in the following: Cramer, R.; Kline, J. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2519.

(6) In the case of ligated C₂F₄, pyramidalization of the carbon atoms arises not because this olefin is an intrinsically better π -acceptor than ethylene but rather because it lowers the energy of the olefin π^* -orbital, giving a better energy match with the metal d-orbitals; see: Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780. Pyramidalization also reduces repulsive interactions between F atoms and the C=C π -bond in C₂F₄; see: Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. Getty, S. J.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4334.

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(1) (a) Dartmouth College. (b) University of Delaware.

(2) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2339.

(3) For recent treatments of this bonding model, see: (a) Albright, T. A.; Hoffmann, R.; Thibault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (b) Mingos, D. M. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, 1983; Vol. 3, Chapter 19, p 1. For discussion of the factors contributing to the activation barriers for propellor rotation of ligated olefins, see ref 3a. Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance*; Jackman, L. M.; Cotton, F. A., Eds.; Academic Press: New York, 1975; p 377.

(4) A compendium of such activation barriers appears in the following: Mann, B. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, 1983; Vol. 3, Chapter 20, p 89.

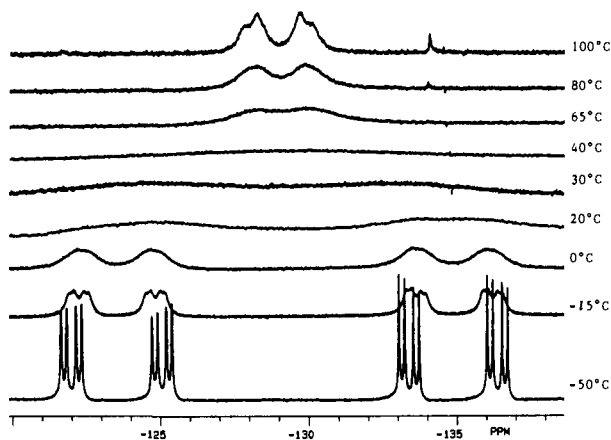
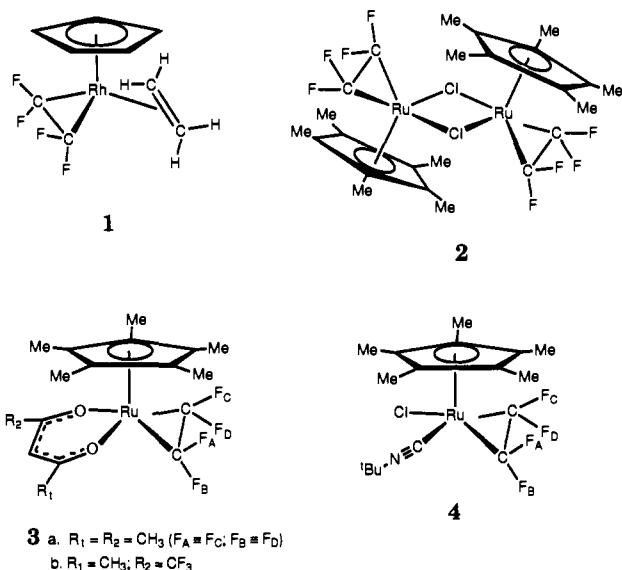


Figure 3. Variable-temperature ^{19}F NMR spectra (282 MHz; toluene- d_8) of the C_2F_4 ligand in **3b**. Chemical shifts are upfield of CFCl_3 .

measured experimentally. Here we report the first example of an (η^2 -tetrafluoroethylene)metal complex which is shown to possess all the structural features associated with a metallacyclopropane, but in which propellor rotation of the C_2F_4 is demonstrably fast on the NMR time scale. The activation barrier to propellor rotation of C_2F_4 is measured for the first time.



The tetrameric ruthenium(II) complex $[\text{Ru}(\text{Cp}^*)\text{Cl}]_4$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)¹² reacts readily with C_2F_4 to afford the dimeric complex **2**.¹³ Treatment of **2** with $[\text{Ti}(\text{acac})]$ ($\text{acac} = \text{acetylacetonato}$)

(8) The 56-MHz ^{19}F NMR spectrum of $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]$ shows an apparent single environment for all four F atoms,⁹ possibly indicative of facile propellor rotation. The molecular structure is consistent with a metallacyclopropane.¹⁰ We now report that the ^{19}F NMR spectrum of this compound at 282 MHz (CDCl_3 ; 20 °C) can be simulated as an AA'BB'X pattern ($\nu_A = -115.1$, $\nu_B = -116.1$ ppm relative to CFCl_3 ; $J_{AA'} = J_{BB'} = -2.4$, $J_{AB} = J_{A'B'} = 104.3$, $J_{AB'} = J_{BA'} = -56.6$, $J_{RHA} = 9.6$, $J_{RHB} = 3.3$ Hz), confirming that rotation is slow on the NMR time scale. A small chemical shift difference is probably the reason for the single F environment reported for the dipivaloylmethane analogue of this acac complex.¹¹ Reference to an apparently low barrier to C_2F_4 rotation appears, without elaboration, in the following: Howard, J. A. K.; Knox, S. A. R.; Terrill, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 640.

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(13) A crystallographic study of **2** confirms its structure and shows the fluoro olefin ligand to be a metallacyclopropane: Curnow, O. J.; Hughes, R. P.; Rheingold, A. L. Unpublished observations. Solubility limitations have precluded detailed NMR studies.

yields the monomeric analogue **3a**,¹⁴ which was characterized by X-ray diffraction.¹⁵ An ORTEP representation of the structure is shown in Figure 2. The geometry of the tetrafluoroethylene ligand in **3a** is almost identical to that found in **1**^{5a} and other C_2F_4 complexes.⁷ The C–C distances are 1.395 (9) Å for **3a** and 1.405 (7) Å for **1**; the average M–C distances are 2.047 (6) Å for **3a** and 2.024 (2) Å for **1**. Structural parameters have been defined by Ittel and Ibers to quantify the nonplanarity of olefin ligands.¹⁶ The only relevant distance comparison is the ratio of M–C to C–C, which is 1.46 for **3a** and 1.44 for **1**;^{5a} all the Ittel–Ibers angles¹⁶ match to within 0.5° in both complexes.¹⁷ The C_2F_4 ligand in **3a** possesses all the structural attributes of a metallacyclopropane.

In toluene (–50 °C) the ^{19}F NMR spectrum of **3a** consists, as expected, of two strongly coupled multiplets, separated by ca. 3000 Hz.¹⁴ On warming, these multiplets coalesce to a single peak. Evidence that this coalescence is not caused by olefin dissociation is provided by the variable-temperature ^{19}F NMR spectrum (Figure 3) of the trifluoroacetylacetonato analogue **3b**,¹⁸ which consists of the expected four multiplets at low temperatures, but which coalesces to two resonances at high temperatures. Propellor rotation interconverts only those fluorine environments trans to one another, whereas dissociation would scramble all environments. Observation of a small spike in the spectrum at –134 ppm (Figure 3) due to free C_2F_4 also confirms that exchange between free and bound olefin is slow on the NMR time scale. Line-shape analysis¹⁹ of the VT-NMR spectra affords values for $\Delta G^\ddagger_{\text{propellor rotation}}$ of 55 ± 2 kJ·mol^{–1} (**3a**) and 53 ± 3 kJ·mol^{–1} (**3b**). These values are at the low end of those normally found for hydrocarbon olefins like ethylene⁴ and are unprecedented for tetrafluoroethylene.⁸

Complex **2** also reacts with *t*-BuNC to afford the mononuclear complex **4**,²⁰ whose ^{19}F VT-NMR spectrum exhibits four resonance to two resonance coalescence similar to that observed for **3b** ($\Delta G^\ddagger_{\text{propellor rotation}} = 59 \pm 2$ kJ·mol^{–1}). Comparison of ν_{NC} for **4** (2176 cm^{–1}) with those for $[\text{Ru}(\text{Cp}^*)\text{Cl}(\textit{t}\text{-BuNC})\text{L}]$ [$\text{L} = \text{PPh}_3$, $\nu_{\text{NC}} = 2059$ cm^{–1}; $\text{L} = \textit{t}\text{-BuNC}$, $\nu_{\text{NC}} = 2078$ cm^{–1} (average of symmetric and asymmetric stretches)]²¹ indicates that, as expected, C_2F_4 is a strongly electron withdrawing ligand compared to a phosphine or isonitrile.

It is clear that, while C_2F_4 acts in character as a strong acceptor ligand in these complexes,⁶ and while that acceptor character affords a metallacyclopropane structure, neither factor precludes

(14) **3a**: 93%, orange crystals; ^1H NMR (C_6D_6) δ 4.99 (s, 1 H, CH), 1.73 (s, 6 H, acac CH₃), 1.31 (s, 15 H, Cp*), ^{19}F NMR (toluene- d_8 , –35 °C, shifts relative to CFCl_3) δ –123.08 (m, $\text{F}_{A,A'}$), –133.62 (m, $\text{F}_{B,B'}$) $J_{A,A'} = 7.7$, $J_{A,B} = J_{B,A'} = -52.0$, $J_{B,B'} = 2.4$, $J_{AB} = J_{A'B'} = 140.1$ Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 187.5 (acac CO), 124.2 (t, $J_{\text{CF}} = 325.5$ Hz, C_2F_4), 102.2 (CH), 100.7 [$\text{C}_5(\text{CH}_3)_5$], 27.9 (acac CH₃), 8.9 [$\text{C}_5(\text{CH}_3)_5$].

(15) Crystal data for $[\text{C}_{17}\text{H}_{22}\text{F}_4\text{O}_2\text{Ru}]$: monoclinic, $P2_1/n$; $a = 8.755$ (3) Å, $b = 14.295$ (4) Å, $c = 14.431$ (4) Å, $\beta = 94.16$ (3)°, $V = 1799.8$ (7) Å³, $Z = 4$, $R(F) = 5.11\%$, $R(wF) = 5.83\%$. Of 5649 data collected (Siemens P4, $2\theta = 4$ –60°, Mo K α , 295 K), 3454 were independent, observed [$4\sigma(F_o)$], and corrected for absorption ($\mu = 9.16$ cm^{–1}). All non-hydrogen atoms were refined with anisotropic thermal parameters.

(16) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(17) For **3a**: $\alpha = 73.9^\circ$, $\beta = 53.0^\circ$, $\delta = 114.5^\circ$, $\gamma = 131.0^\circ$. For **1**:^{5a} $\alpha = 74.3^\circ$, $\beta = 52.8^\circ$, $\delta = 114.3^\circ$, $\gamma = 131.4^\circ$. See ref 16 for definition of these angles.

(18) Prepared from **2** and the corresponding Ti salt. **3b**: orange crystals; 80%; ^1H NMR (C_6D_6) δ 5.46 (q, $J_{\text{HF}} = 0.4$ Hz, 1 H, CH), 1.53 (s, 3 H, CH₃), 1.21 (s, 15 H, Cp*); ^{19}F NMR (toluene- d_8 , –50 °C): δ –77.85 (s, CF_3), –122.81 (dd, F_B), –125.84 (dd, F_D), –134.10 (dd, F_C), –136.07 (dd, F_A), $J_{AB} = 141.3$, $J_{AC} = 0.0$, $J_{AD} = -53.5$, $J_{BC} = -54.3$, $J_{BD} = 0$, $J_{CD} = 136.6$ Hz. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{F}_7\text{O}_2\text{Ru}$: C, 41.72; H, 3.91. Found: C, 41.53; H, 4.01.

(19) The original version of the line-shape analysis program was written by D. A. Kleier and G. Binsch (*J. Magn. Reson.* **1970**, *3*, 146–160; Program 165, Quantum Chemistry Program Exchange, Indiana University). Modifications are described in the following: Bushweller, C. H.; Bhat, G.; Lentendire, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65–73.

(20) **4**: yellow crystals; 88%; IR (CH_2Cl_2) ν_{NC} 2176 cm^{–1}; ^1H NMR (C_6D_6) δ 1.56 (s, 15 H, Cp*), 0.91 (s, 9 H, *t*-Bu); ^{19}F NMR (toluene- d_8 , –20 °C) δ –109.54 (ddd, F_A), –119.50 (dd, F_B), –123.80 (ddd, F_C), –125.34 (dd, F_D), $J_{AB} = 140.8$, $J_{AC} = 4.2$, $J_{AD} = 48.6$, $J_{BC} = 50.3$, $J_{BD} = 0$, $J_{CD} = 142.4$ Hz. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{ClF}_4\text{NRu}$: C, 44.89; H, 5.32; N, 3.08. Found: C, 45.57; H, 5.78; N, 3.59.

(21) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1987**, *322*, 221.

facile propellor rotation. As emphasized previously by others,³ there should be no correlation between acceptor properties of an olefin and the activation barrier to this form of stereochemical nonrigidity; differences in the barrier may arise from variations in the cylindrical properties and energies of the orthogonal π -orbitals presented to the olefin by the metal fragment, differences in orbital overlap along the rotational pathway, and other attractive or repulsive interactions in the transition state. Theoretical studies of the molecules discussed herein are in progress.

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Supplementary Material Available: Structure determination, data collection, and solution and refinement summaries and tables of atomic coordinates and isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for complex **3a** (6 pages); observed and calculated structure factor tables for complex **3a** (19 pages). Ordering information is given on any current masthead page.

(Et₃P)₄Fe₄Te₄: An Intermediate between Molecular Reagents and Solid-State Products

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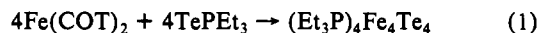
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We have reported a number of reaction sequences in which molecular reactants are converted into extended inorganic solids.¹ Our goals have been to design simple and general methods for the transformation of molecules to solids and to learn as much as possible about the pathways connecting the two. In this paper we report the synthesis of a mixture of β - and ϵ -FeTe and the isolation and characterization of (Et₃P)₄Fe₄Te₄, a cluster compound that is formed directly from the molecular reagents and that is subsequently converted to the solid products.

Compounds of low-valent transition metals react with phosphine tellurides¹⁻⁴ to form metal-tellurium bonds. We sought to extend this synthesis methodology and became particularly interested in the chalcogenides of iron because of the remarkable and confusing magnetic properties of the bulk materials.⁵ (One hope is that

the structure and behavior of iron-chalcogen clusters might shed some light on the properties of the extended solids.) We therefore looked for a low-valent complex of iron with which Et₃PFe might be expected to react. Fe(COT)₂ was an attractive candidate.⁶ The metal is easily oxidized,⁷ and the COT ligands are molecular and could be expected to fall off the metal^{7,8} on reaction with phosphine telluride. We find⁹ that this is the case. Fe(COT)₂ reacts quickly at room temperature in toluene with Et₃PFe to lose the COT ligands and yield the cluster compound (Et₃P)₄Fe₄Te₄ (eq 1). We determined the structure of this molecule crystallographically,¹⁰ and a drawing of the molecular structure is shown in Figure 1.



The molecule has cubic symmetry and therefore has only one independent Fe, Te, and P atom and two independent C atoms. The core of each molecule is a tetrahedron of Fe atoms with an Fe-Fe distance of 2.623 (4) Å. Each face of the tetrahedron is capped with a single Te atom, the resulting Te₄ tetrahedron having a characteristic Te-Te distance of 4.343 (1) Å. The structure is capped and completed by a phosphine ligand at each Fe. The Fe-Te distance is 2.609 (1) Å. This is in the range normal for Fe-Te bonds^{11,17a,b} and implies that the bonding in the cluster is dominated by the direct Fe-Te interactions. It is significant, however, that the Fe-Fe distance is only 0.14 Å longer than the nearest-neighbor distance in elemental Fe. This suggests the presence of a substantial stabilizing interaction among the Fe atoms, particularly when compared to other [FeTe]₄ compounds (see below).

The [FeTe]₄ core may be viewed as a severely distorted cube. In this sense this compound is a member of the large family of iron-chalcogen cubanes.¹²⁻¹⁷ One [FeTe]₄-based solid^{17d} and two other molecular [FeTe]₄ complexes (of the type [(PhE)₄Fe₄Te₄]³⁺, E = S, Te) have been structurally characterized to date.^{17a,b} The present compound differs from these in having only neutral

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(7) Gerlach, D. H.; Peet, W. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 4545.

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(9) Preparation of [(Et₃P)FeTe]₄: All manipulations were carried out under an inert atmosphere. Fe(COT)₂ (1.0 g, 3.8 mmol) was dissolved in toluene (30 mL) to which Et₃P (1.7 mL, 11.5 mmol) had been added. In a separate vessel, Et₃PFe (0.93 g, 3.8 mmol) was dissolved in 10 mL of toluene. The Te-containing solution was added to the Fe-containing solution at room temperature. After 16 h, the solid which had deposited was separated by filtration, washed (2 × 5 mL of pentane), and dried. Yield: 0.82 g (0.68 mmol = 72%). Anal. (C₂₄H₆₀Fe₄P₄Te₄) C, H, Fe, P, Te. The material was crystallized from 10/1 toluene/Et₃P, cooling slowly from 80 to 90 °C. The UV-visible absorption spectrum of this material shows broad, featureless absorption across the visible region. The cluster is not sufficiently soluble for NMR spectroscopy.

(10) Crystal data: space group *I*4̄3m; cubic; *a* = 12.9548 (5) Å; *V* = 2174.16 (8) Å³. Details of the crystallography are included in the supplementary material.

(11) Typical values for Fe-Te bond lengths in molecular compounds other than [FeTe]₄ clusters range from 2.47 to 2.59 Å. See: Compton, N. A.; Errington, R. J.; Normant, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91. In β -FeTe (PbO structure type, Fe rich), the Fe-Te distance is 2.62 Å;^{5a} in δ -FeTe (NiAs structure type, Te rich), the Fe-Te distance is 2.698 Å.^{5a}

(12) See, for example: (a) Holm, R. H.; Ciurli, S.; Weigel, J. A. *Prog. Inorg. Chem.* **1990**, *38*, 1. (b) Weigel, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 4184 and references therein.

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